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PAINT RESEARCHES

AND

THEIR PRACTICAL APPLICATION

BY

HENRY A. GARDNER

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WASHINGTON, D. C.
PRESS OF JUDD & DETWEILER, INC.
1917

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DEDICATION

TO THE

PAST AND PRESENT MEMBERS OF THE
EDUCATIONAL BUREAU
OF THE PAINT MANUFACTURERS' ASSOCIATION

WHO HAVE GIVEN UNSELFISHLY OF THEIR TIME TO SOLVE PROBLEMS
THAT HAVE CONFRONTED THE INDUSTRY AND WHO HAVE ENCOURAGED INVESTIGATIONS WHICH MIGHT BROADEN
THE GENERAL KNOWLEDGE OF PAINT,
THIS BOOK IS DEDICATED

372176

PREFACE

The work undertaken by the writer during the past six years for the Educational Bureau of the Paint Manufacturers' Association of the United States has been conducted at The Institute of Industrial Research at Washington. During this period of time considerable sums of money have been spent on investigations made to determine the usefulness of various materials which might find employment in the industry. While many of the results have been communicated to the manufacturers, they have never been placed in a form for ready reference. It is hoped, therefore, that this volume, with its complete index and many illustrations, will prove useful for this purpose, and at the same time serve as a guide to the student who desires to be in touch with recent work on the technology of paint.

WASHINGTON. D. C., *February* 1, 1917.

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CHAPTER I.

THE GROWTH OF THE PREPARED-PAINT INDUSTRY AND ITS RELATION TO THE WORK OF THE PAINTER.

The writer has often been asked to cite some of the conditions which are responsible for the recent development of the paint industry of this country and the ever-growing demand for those higher-grade paints which are prepared upon scientific principles. That some change has been wrought, which is responsible for this condition, is evident, for the amount of paint made by the grinder of early days is insignificant when compared with the amount made in modern times.

Painters who at one time mixed all of their own paints; dissolved and melted the resins for their varnishes; boiled sufficient oil for their requirements, and prepared by hand enough colors for any certain piece of work, are now purchasing many of these products in large quantities in prepared form. This one change has led to an enormous growth of the grinding business. It is possible that one of the factors which might be held responsible for this change could be looked for in the conditions now surrounding the employment of painting labor. Master painters have often referred in their discussions at association meetings to the many years of apprenticeship which they served, either in this country or abroad, while learning their trade. They have, moreover, loudly lamented, and with just cause, the gradual disappearance of this same apprenticeship system which was responsible for the production of first-class painters of all-around general ability. The writer has even heard statements made by prominent masters in the trade that great difficulty is now experienced in getting one "brush hand" out of twenty men, who is really capable of mixing every kind of color or paint in a satisfactory manner. If these statements are true, it is to be assumed that a large percentage of the workmen now employed in applying paint have never served an apprenticeship, and have never acquired that information and skill which is necessary to qualify them as fore-

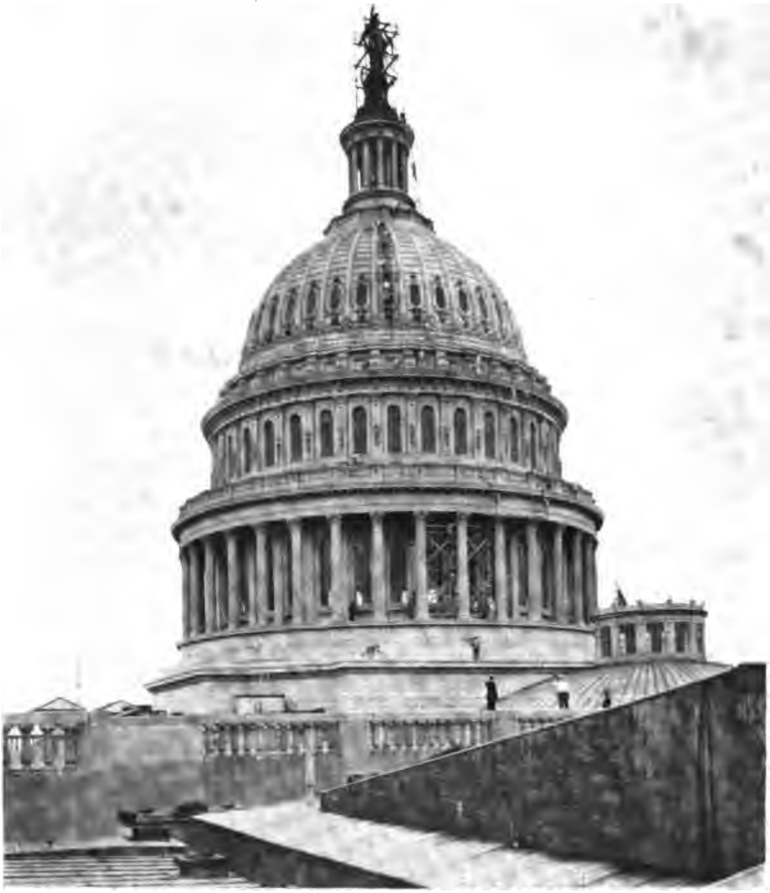


FIG. 1.
View of dome of U. S. Capitol during painting. Five thousand gallons of paint* required.

men able to mix paints, colors, varnishes, and stains for every class of exterior and interior decorating. Some of the factors which have contributed to this situation are the changed social and economic conditions, the rapid growth of communities, and the ever-present desire for more speed in everything that is done. As a result, the busy master painter himself is unable to produce, as in the days of old, all of the paint necessary for a big job, nor has he enough competent men in his employ to do so. The day of color grinding on slab and muller and the age of "one paint for all purposes" has therefore gradually passed to an age where the painter has found it necessary to have manufactured for him many of his products in prepared form. Although the lack of apprenticeship-trained men able to mix such products has done much to bring about this condition of affairs, there are other factors which must be considered as having a contributory effect. The production of thousands of gallons of a certain delicate tint of wall paint or enamel, or the making of an equal quantity of interior varnish stain and color for the decoration of one of the enormous office structures of modern times, is a feat not to be accomplished in an economical manner in any small paint shop. The capacity and facilities of modern factories and the use of high-powered machinery, guided by trained experts, are now required for such a task.

---

* Paint composed of basic sulfate, white lead, and zinc oxide base in linseed oil.

Out of these conditions there has grown up in this country one of the most important industries on the American continent—an industry employing thousands of men and representing millions in capital. It is fair to state, however, that the early history of this industry is not one of which the American people may be proud. The products of those days were, according to report, adulterated in many instances, badly made in others, and generally of a nature to create prejudice against their use among the more scrupulous of the painting fraternity. It should be noted, however, that these conditions came largely as the result of an astounding lack of technical knowledge among manufacturers as to the properties of the raw materials which they used. There was, in those days, no chemical control of such materials to determine their purity. Oil bought as linseed oil, even by the grinder, may have been grossly adulterated. Lead purchased as pure may have been free of such a metal. If the manufacturer, therefore, did not possess means of selecting pure materials, and did not know how to properly mix and grind the raw materials entering into the composition of paint, there was but little chance for the painter to become enthusiastic in the use of these early products which were then classified as "ready-mixed paints."

With the advent of the twentieth century there came a change in this state of affairs as a result of the application of science to the industry. The making of paint and varnish products in a haphazard manner by untrained men, through closely-guarded secret processes, was stripped of its secrecy and its false importance. The raw materials entering into paints immediately became the subject of exhaustive study. Their chemical composition, physical properties, and actual value were determined with accuracy and kept subject to careful chemical control. Traditional beliefs with respect to certain products were shown in many cases to be based upon ignorance. Newer commodities were brought into the field, gradually developed, and their value proved. The principles of science were applied to the various processes of manufacture. Newer and better-designed machinery and equipment were provided. Savings were effected at various places and wastes were largely eliminated. As a result of these changes the industry forged rapidly ahead until the United States became the leader of all nations in actual output and in quality of output.

The master painter may have looked askance in many instances at this wonderful development in the manufacture of prepared-paint products, thinking that it was robbing him of the opportunity of making all of his own products, and in this way decreasing to some extent the scope of his work. This belief, however, is incorrect, for it is an actual fact that the greater the amount of paint made by the grinder the greater will be the amount of paint applied by the painter. To illustrate this point, it is only necessary to point to the perfectly enormous amount of flat wall paint which is today made by the grinder and applied by the painter. Ten years ago the interior walls of buildings were generally left bare and in an unsightly condition. The production by the manufacturer, through the use of newer pigments and oils, of a wall paint which would dry to a soft, velvety flat finish, and which could be easily and economically applied, created a wider desire for wall decoration. People started to paint the walls of their homes, their offices, and their factories. With this newly-created demand for the newer paints came a proportionate demand for the services of the painter to apply them. In creating a market for their paints, the grinders also created a market for the services of the painter. For every million dollars' worth of paint sold, there came requirements for at least two million dollars' worth of painting labor, since the cost of applying paint is always at least twice the cost of the paint applied.

The production of the newer products by the manufacturer, and his efforts to create with the ultimate consumer a demand for such products, constitutes, therefore, a direct call for the services of the painter, and should be encouraged by him wherever possible.

CHAPTER II.

THE WHITE-PIGMENT INDUSTRY.

Of the white pigments consumed in the paint-grinding trades, only a relatively small proportion is represented by those known as natural earth pigments which are prepared by crushing, grinding, and washing various minerals.* Such pigments will not be considered in this chapter, which bears wholly upon those pigments made by chemical or metallurgical processes from ores having a lead or zinc base, and referred to herein as opaque white pigments.

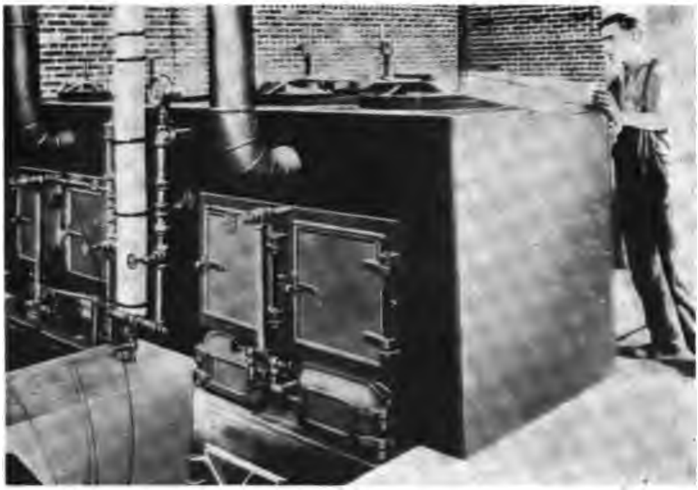


FIG. 2.
Lead melting-pots in white-lead factory.

Five years ago the opaque white pigments produced in the United States amounted to about 230,000 tons, valued at approximately $25,000,000. The writer's estimate for the year 1916 shows a production of approximately 370,000 tons, having a value of over $70,000,000. This tremendous growth of the industry is not to be ascribed to any very marked increase in exports or to other conditions consequent upon the unsettled situation that prevails abroad and which might exert an expansive force on our trade thermometer. While, of course, such conditions would naturally increase the demands arising as a result of the growth of certain communities, it is the writer's opinion that the prevailing activity in the pigment world is largely due to the rapidly developing appreciation of the value of those products in which pigments are used. Let us now consider the five important white pigments produced in this country and their application in the paint industry where the largest amounts are used. Of these, the oldest will receive first consideration.

---

* For data on the natural earth pigments, see "Production of Mineral Paints in 1914," U. S. Geological Survey; also Consular Report 56, "Foreign Trade in Paints and Varnishes." U. S. Department of Commerce.

TABLE I.

An Estimate of the Production of the Opaque White Pigments in the United States.

		1911.‖		1916.	
		Quantity.	Value.	Quantity.	Value.§
		Tons.		*Tons.*	
Chemical process	Basic Carbonate-White Lead	132,612*	$17,393,241	160,000†	$28,800,000
	Lithopone	16,866	1,243,108	75,000	16,500,000
Fume process	Basic Sulphate-White Lead Zinc Oxide Leaded Zinc Oxide.	80,611	7,343,762	139,000‡	28,150,000
Total		230,089	$25,980,111	374,000	$73,450,000

*Of this amount, 106,778 in oil, balance dry.

† Of this amount, 130,000 in oil, balance dry.

‡ Of this amount, Basic Sulphate-White Lead and Leaded Zinc constitute 43,000 tons, Zinc Oxides 96,000 tons.

§ White Lead Pigments and Leaded Zinc estimated at $175 per ton, American Process Zinc Oxide at $190, French Process Zinc Oxide at a higher price, and Lithopone at $210.

‖ 1911 figures from U. S. Geological Survey Bulletin, Production of Mineral Paints for 1914.

Basic Carbonate-White Lead.—The date of the first commercial production of corroded white lead in the United States has been recorded as 1807, and at the present time there are two large manufacturing organizations and several smaller individual corroders, the plants being well distributed throughout the country. The production of the pigment in the various factories depends mainly upon the use of two distinct processes, which are described later on in the text.

There is probably no commercial pigment that has a pedigree quite as long as that held by corroded white lead, and its family history is indeed interesting. Many records of its use in ancient times have been found, and the following has been quoted in the excellent paper on White Lead by Klein:**

> "One of the earliest records of white lead is to be ascribed to Xenophon (430-355 B. C.), who in 'Aeconomicus'* records the use of 'cerussa' as a cosmetic. Church† states that a face powder or cosmetic, found in its original pottery box, of about B. C. 400, in the neighborhood, proved to be a mixture of white lead and whitening."

It is evident from this report that some of the modern paint mixers are not the only ones to understand the art of mixing earth pigments with lead, but whether it was done in those days for purposes of profit or to lessen the toxic effect of the pigment, is not known. Later on, however, in the fourteenth century, it is evident that certain pigments were looked upon with suspicion, as the following reference also from Klein will indicate:

> "Cennino Cennini‡ states that the ladies of Florence were prone to heighten their beauty by the application of white lead and other pigments, and in a homily warns ladies in general against the practice."

Since it is not intended in this chapter to deal with the toxic effect of pigments, those who desire further information on this subject may refer to the publications noted below.§ That the so-called ancients knew how to make real white lead is also shown by Klein in his quoted passage from Theophrastus (373-287 B. C.): ||

**"The Manufacture of White Lead." C. A. Klein, Chief Chemist, Brimsdown Lead Co., L't'd. Presented before the Paint and Varnish Society of London, December 4, 1913.

* Xenophon, quoted by Hofmann, "Das Blei."

† Church, "Chemistry of Paints and Painting," 127. 1901, Seeley, London.

‡ Cennini, "Treatise on Painting," etc., translated by Mrs. Merrifield. London, 1845, p. 51.

§ Bulletin 188, Department of Labor; also "The Toxic and Antiseptic Properties of Paints." H. A. Gardner, Bulletin 41, Scien. Sec., Paint M'f'rs' Ass'n of U. S.

|| History of Stones, p. 223.

> "Lead is placed in earthen vessels over sharp vinegar, and after it has acquired some thickness of a sort of rust, which it commonly does in about 10 days, they open the vessels and scrape it off, as it were in a sort of foulness; they then place the lead over vinegar again, repeating over and over again the same method of scraping it till it has wholly dissolved. What has been scraped off they then beat to a powder, and boil for a long time, and what at last subsides to the bottom of the vessel is 'ceruse.'"

This old method undoubtedly produced a white lead carbonate, and it is interesting to note that the clay pot method is still in use today, but, of course, in a much more highly developed condition and now known as the stack or Old Dutch process. Moreover, this process is responsible for a greater tonnage of product than all of the newer processes combined. This fact is indicated by Klein's figures (1914) on the lead production of the world, as quoted below:

TABLE 2.

Quantity of White Lead Produced by Principal Producing Countries.

Estimated Total Production, 275,000 Tons Annually.

	English tons, dry.
United States	120,000
England	55,000
Germany	36,500
France	22,000
Belgium	15,000
Russia	14,500
Italy	4,500
Holland	2,500
Spain	2,500
Canada	2,500

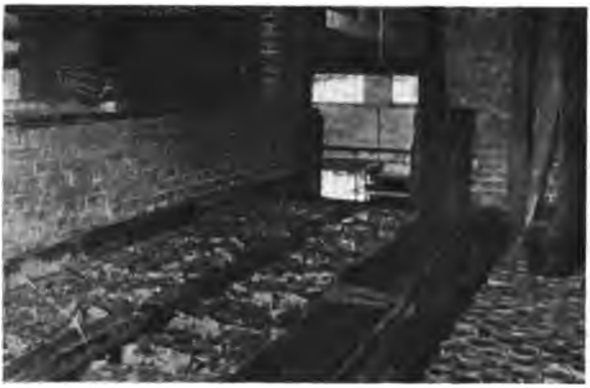
TABLE 3.

Approximate Quantities Produced by Various Processes.

Stack	180,000 tons
Chamber	45,000 "
Miscellaneous	50,000 "

Comparison of these figures should be made with the figures given by the present writer in Table 1.

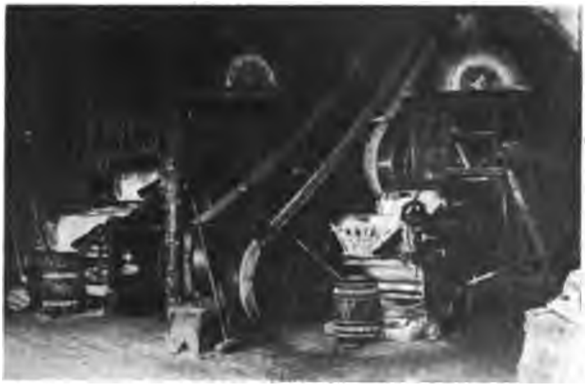
It might be desirable to describe herein very briefly the various processes by which white lead is manufactured at the present time.



Courtesy A. S. Jennings and Messrs. Foster, Blackett, and Wilson

FIG. 3.

"Blue beds" of lead strips before corrosion at English factory.



Courtesy A. S. Jennings and Messrs. Foster, Blackett, and Wilson

FIG. 4.

Grinding white lead in oil at an English factory.

In the stack process, a series of units consisting of clay pots surrounded with tan bark and containing cupped acetic acid at the bottom, are filled with buckles or discs of metallic lead. The pots are then covered with boards upon which are stacked subsequent layers of pots. Fermentation of the tan bark raises the temperature of the stack, facilitating the action of the acid upon the lead, forming the acetate which in the presence of the carbon dioxide evolved during the fermentation of the bark is transformed into the white basic carbonate. The process requires about three months' time, and when the stacks are finally stripped, the white lead is broken up, ground, washed, and prepared for the market. In the chamber process, which is used on the European continent quite widely, and especially in Germany, large brick corroding chambers are used, in which strips of lead are hung from horizontal girders; a mixture of air, acetic acid, steam, and carbon dioxide being blown into the chambers through inlets in the floor. In less than two months' time the corrosion is complete, the dry white lead being removed and treated in the usual manner. In the Carter process, as used in the United States, metallic lead is granulated and placed in large revolving wooden drums; acetic acid and water being sprayed on the mass. Carbon dioxide gas is passed into the cylinders and agitation continued for a period of from six days to two weeks. The white lead produced is thoroughly levigated and then dried. In the Rowley or mild process, lead is melted and sprayed by means of air or steam to the form of a very fine metallic dust into a

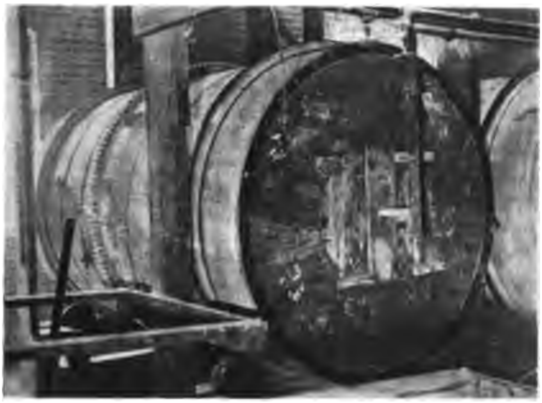
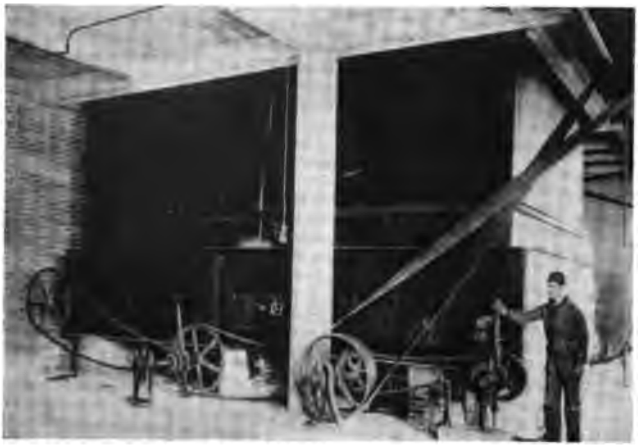


FIG. 5.
Revolving cylinders used in making quick process white lead.

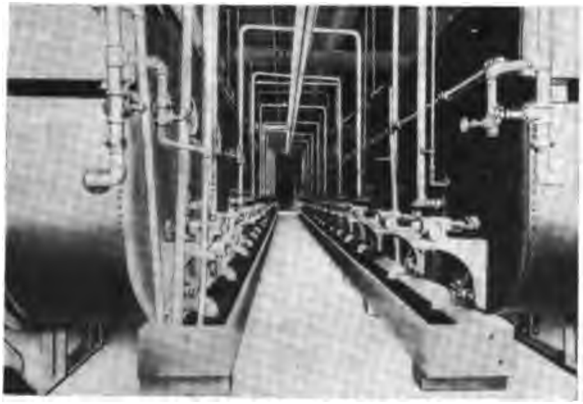
large iron chamber luted with water at the bottom. The mass is then agitated in the presence of air to produce the hydrate of lead,



Courtesy C. S. Neal

Fig. 6.

Steel chamber used in making mild process white lead.



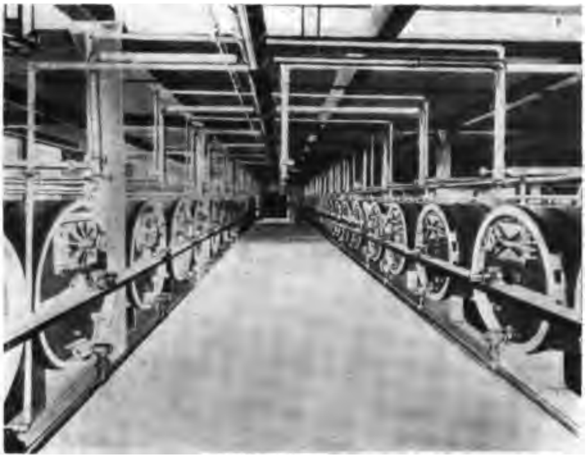
Courtesy C. S. Neal

Fig. 7.

Agitation tanks for mild process lead.

and then placed in revolving cylinders and treated with carbon dioxide gas. Basic carbonate of lead is produced in two or three days' time. Although only a small amount of white lead is made by this process, that produced is generally of a good grade. Other processes, including the electrolytic process, have been proposed and experimented with, but not with any great degree of success.

The enormous tonnage of corroded white lead produced and sold in the United States indicates the extent to which this valuable pigment is consumed in the form of paint. It is used as the base of the majority of white and tinted paints and generally in admixture with a substantial percentage of zinc oxide or other pigments in which form the best results are obtained. For reports on the comparative wearing value of such paints, the reader is referred to the publications noted below.* While it is probable that a still greater quantity of corroded white lead would be in use today if other white pigments were not available, we must remember that even the enormous strides made in the use of the newer pigments have apparently only served to help fill the increased demand that



Courtesy C. S. Neal

FIG. 8.

Carbonating cylinders for mild process lead.

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* Bulletins of the Scien. Sec., Paint M'f'rs' Ass'n of U. S.: No. 34. "Report of the 1912 Inspection of the Atlantic City Wooden Test Fence, Including the Repairing Tests and the New Tests"; No. 35, "Report of the 1912 Inspection of the Pittsburgh Test Fence," etc.: No. 36, "Report of Inspection of the Tennessee Test Fence."

has arisen for white pigments, and there has been, therefore, an increased production of each type. With the new uses for pigments that are being developed in various industries, there will probably be a continuation of the present growth of production, and the different pigments will be used for the purposes for which their individual characteristics best fit them.

Basic Sulphate-White Lead.—Sublimed white lead or basic sulphate-white lead has become one of the most important and valuable paint pigments used at the present time. Its history dates back to the experiments of Lewis and Bartlett made about the year 1872. Mr. Bartlett has told the writer that while working around a zinc smelter in Bethlehem, Pennsylvania, he once picked up a beautifully crystallized sample of galena (lead sulphide ore). While passing a calcining or desulphurizing furnace he threw the specimen into the red-hot furnace and immediately it ignited and passed off as a white fume. He at once conceived the thought that this sublimed product might be white lead, and immediately began experiments to determine whether white lead could be produced by this fire process.

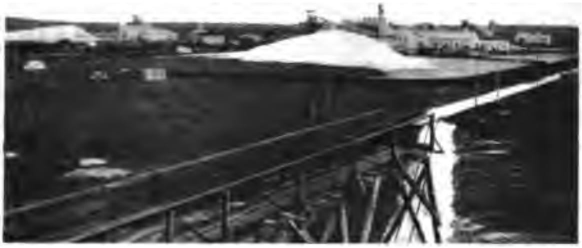
Courtesy Dr. J. A. Schaeffer

FIG. 9.

Mining lead ore at depth of 270 feet.

Great advances have since occurred in the manufacture of this interesting pigment which was originally produced in commercial amounts by the Picher Lead Company. It now finds wide use as a constituent of nearly every kind of paint. Its extreme stability, amorphous nature, great fineness, hiding power, durability, and relatively non-poisonous properties have in many instances given it preference over the corroded form of white lead.

At the present time the pigment is made at Joplin, Missouri, and Collinsville, Illinois, from galena ore which contains some blende or zinc sulphide. The ore, after being crushed and concentrated, is charged into specially constructed furnaces where it is subjected to intense heat, the metal content being vaporized and oxidized to a white fume pigment. This pigment in its vaporous form is carried through a series of gooseneck cooling pipes where the oxidation is completed, and finally through a long metal flue for cooling purposes, being deposited at the end of the system in fabric bags. It consists of a true basic sulphate of lead, and its average composition will show it to contain approximately 16 per cent of chemically combined lead oxide, the balance being lead sulphate and generally from 1 per cent to 5 per cent of zinc oxide.

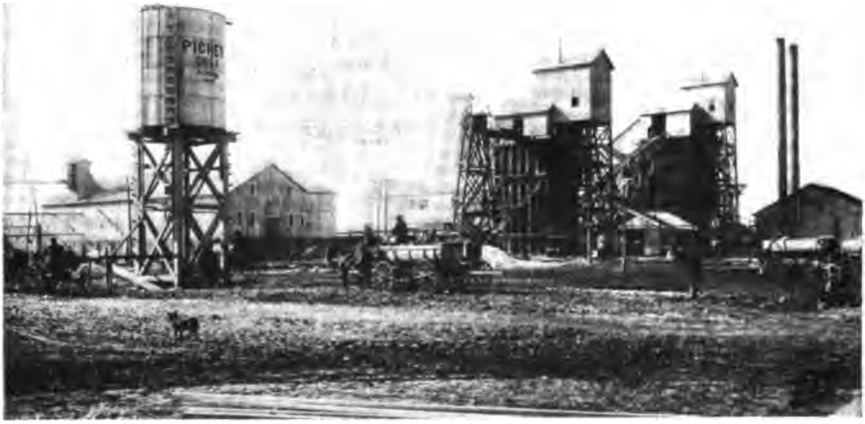


Courtesy Dr. J. A. Schaeffer

FIG. 10.

View of large pile of tailings from which pigment ore has been recovered.

Most remarkable results have been obtained with this pigment when made into paints that have been used upon exterior surfaces of wood, iron and cement, as some of the references below will indicate. It is also coming into considerable use for the manufacture of interior paints of various kinds.



Courtesy Dr. J. A. Schaeffer

FIG. 11.

View of mines from which pigment ores are taken.

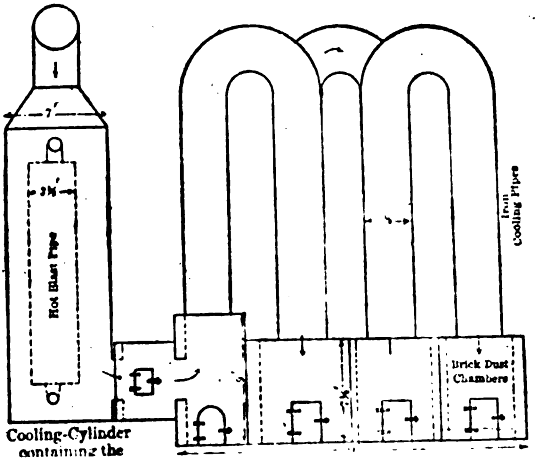


FIG. 12.

Goosenecks used in making fume pigments.

In the last published report on the Atlantic City wooden test fence,* it was stated that: "The white paints made of zinc oxide and basic sulphate-white lead * * * were giving exceptional service." This report was made after the tests had been exposed to the severe conditions prevailing at the seacoast for five years, with one repainting. In a similar report† on the Nashville wooden test fence, after two years' exposure, it was stated that: "Basic sulphate-white lead presented a surface free from checking or alligatoring, this result being in accord with the findings from previous field tests." At Pittsburgh, excellent results were also obtained from basic sulphate-white lead, the mixed pigment paints containing this pigment being especially resistant to darkening or discoloration.‡ In the Atlantic City steel panel tests, sublimed white lead was the only white pigment among the pigments receiving the ten highest average ratings in the inspections of 1910, 1911 and 1912.§

W. G. Scott in his book entitled, "White Paints and Painting Materials," comments on sublimed white lead as follows:

> "One of the prominent features of sublimed white lead is its extreme fineness. The texture of a pigment may be *crystalline*, or *amorphous*. Sublimed white lead belongs to the latter class, and owes its great covering capacity to its amorphous condition. Sublimed white lead on account of its fineness will stand a great amount of extension, and may be safely mixed with nearly any color.
>
> "Sublimed white lead of the average composition contains about 69.78 per cent of metallic lead; but, unlike carbonate of lead, which is easily reduced to metal under the blow-pipe, it is almost impossible to reduce the sublimed product without a powerful reducing flux; hence, it may be said to be practically fireproof.
>
> "The specific gravity of sublimed white lead ranges from 6.000 to 6.400, a gravity of 6.200 being a true average, consequently a cubic foot of the pigment in compact form, *i. e.*, considered as a solid, will weigh about 387 pounds; in similar manner, a gallon (231 cu. in.) of solid material would weigh 51.69 pounds.

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* Bulletin 34, Scien. Sec., Paint M'f'rs' Ass'n of U. S., "Report of the 1912 Inspection of the Atlantic City Wooden Test Fence."

† Bulletin 36, Scien. Sec., Paint M'f'rs' Ass'n of U. S., "Report of Inspection of the Tennessee Test Fence."

‡ Bulletin 35. Scien. Sec., Paint M'f'rs' Ass'n of U. S., "Report of the 1912 Inspection of the Pittsburgh Test Fence."

§ Circular 35, Scien. Sec., Paint M'f'rs' Ass'n of U. S., "Notes on Prepared Paints for Metal Surfaces."

> "Sulphur fumes, coal gas, smoke, and other obnoxious gases have very little effect upon sublimed white lead, a long period of time being required to perceptibly darken the paint. Sublimed white lead is occasionally used alone as a paint, but more often as the principal ingredient in what is known as 'composite paints.' When ground alone in oil to produce a moderately stiff paste, sublimed white lead requires about 9¾ per cent of oil; this is in nearly the ratio of 100 pounds of dry lead to 1¼ gallons of oil."

From time to time, there have been discussions as to the propriety of the term "white lead" as applied to the sublimed product. That basic sulphate of lead has as much right to the name as basic carbonate of lead, is now generally recognized. This is indicated in recently issued Circular 42 of the Paint Manufacturers' Association of the United States, from which the following is quoted:

FIG. 13.

Largest plant in the world for the production of sublimed lead pigments, at Joplin, Mo.

> "These definitions and the accompanying nomenclature have been prepared by the Educational Bureau in answer to a demand for an authoritative standard nomenclature, for use in connection with formulas, labels, specifications, etc., when required. This would apply, for example, to the branding of the several forms of 'white lead,' the recommendation being that all types of the basic carbonate be designated 'basic carbonate white lead,' and all forms of the basic sulphate, 'basic sulphate white lead.'

"The effect of the general adoption of this nomenclature will be to eliminate the existing confusion and replace it by definite terms applicable to definite products.

"This nomenclature was recommended to the association in October, 1915; referred to the membership by mail vote; revised in accordance with suggestions of members; and adopted by unanimous vote at the annual meeting on November 17th, 1916.

"Proposed Nomenclature of the Important Raw Materials Used in Paint.

Manufacturer's title or trade-names in common use.	Suggested nomenclature.	Remarks.
White Lead Corroded Lead Corroded White Lead Carbonate of Lead Basic Lead Carbonate Basic Carbonate White Lead Hydrate of Lead Hydrocarbonate of Lead Lead Carbonate Carbonate White Lead	Basic Carbonate White Lead	It is optional whether additional information appears in connection with the title to indicate whether the material represents 'Old Dutch Process' or a 'Quick Process' pigment.' "
White Lead Sublimed Lead Sublimed White Lead Basic Lead Sulphate Sulphate of Lead Basic Sulphate White Lead	Basic Sulphate White Lead	

Zinc Oxide.—The use of zinc oxide best known to the general public is its employment in the form of a paint pigment. In this form it has very much the same physical action as metallic zinc. The latter will convey to some other metals, when used in alloys, the required degree of hardness. Analagously, zinc oxide will convey to lead paints the property of becoming sufficiently hard to resist some peculiarly inherent forms of decay and discoloration. *Without entering into a lengthy discussion of this subject, it is significant to refer to the fact that the use of zinc oxide is universal with the*

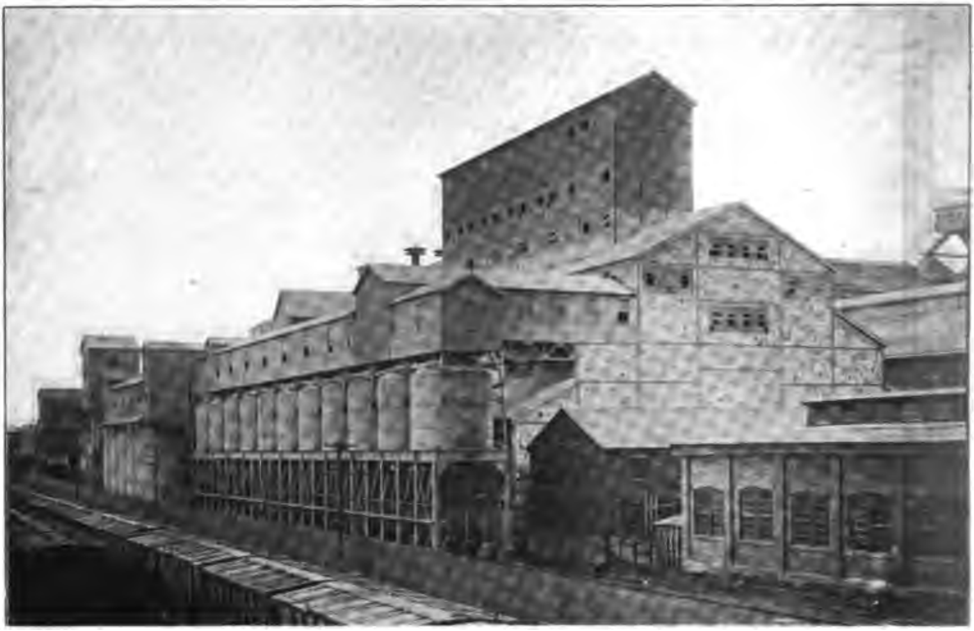

Fig. 14.
Retreatment house for zinc ores at Franklin, N. J.

paint manufacturers of the United States and it is rapidly becoming standard practice with the painting craft to use zinc oxide in nearly all interior and exterior paints.

A search of the literature shows that Courtois* made zinc oxide regularly on a large scale in 1781, and there are records showing that in 1784 this pigment was used extensively in artists' paints. Its

Fig. 15.
Panoramic view of zinc oxide works at Palmerton, Pa.

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* Ann. des Arts et M'f'g, vol. II (September, 1800).

production by a metallurgical process, however, dates back only to 1834 when Sorel, while experimenting on galvanizing metal, discovered that the white powder formed at the edge of the zinc pots consisted of zinc oxide. Later records, about 1841, show the commercial production of the pigment by Leclaire and its successful use in house paints. In 1848 the New Jersey Zinc Company, when experimenting on Franklinite zinc ore, developed a direct process for making zinc oxide, and this process is now responsible for the major part of the zinc oxide produced. Mr. George C. Stone, chief metallurgist of the New Jersey Zinc Company, has written an interesting history of the development of the process, which is presented below.*

> "An entirely new process of making oxide of zinc direct from the ore was invented in the early '50s, and three patents were taken out in 1855, by Jones, Burrows and Wetherill, on almost identical lines. Jones was an officer of the New Jersey Zinc Company; Wetherill was the superintendent of the paint-grinding department, and Burrows was a workman employed by the Passaic Chemical Company, whose works adjoined those of the New Jersey Zinc Company, and some of whose furnaces were on its property. Burrows states that one night the flue from one of the furnaces that he was tending leaked, and he covered the hole with a piece of grate bar, throwing a shovelful of refuse on it. The refuse proved to be a mixture of coal and zinc ore and, the heat of the flue being sufficient to light it, Burrows soon noticed a cloud of zinc oxide coming off. He built a small furnace and repeated the experiment, and when he found that it worked again, showed it to the officers of the New Jersey Zinc Company, among whom were Wetherill and Jones.
>
> "Col. Wetherill proposed to Burrows that they work up the invention together, as Burrows had not the money to do so on his own account. The result was that three people applied for and obtained patents for substantially the same thing in the same year. Wetherill also took out patents for improvements in 1855-6-7-9 and two in 1868. The New Jersey Zinc Company acquired the patents of Jones and Burrows, but could not agree on terms with Wetherill. The latter shortly afterwards sold a license to use his process to the Passaic Zinc Company. Both the New Jersey and the Passaic companies put the process in operation, as it proved to be a great improvement on those

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*"The History of Zinc Oxide." Geo, C. Stone.

previously used. Everything went quietly until the Wetherill patent had nearly expired, when he brought suit against the New Jersey Zinc Company for infringement and accumulated profits. The suit that followed was long and hotly fought on both sides. The final decision of the court was that the furnace was Burrows' invention and the process Wetherill's and that half the profits were due to each. As the Zinc Company owned the Burrows' patent, it was obliged to pay half the increased profit due to the use of the invention, to Wetherill. The decision seems a very fair one, as while the original idea appears to have been Burrows', he had not sufficient knowledge or skill to develop it and make a working process of it. The latter was done by Wetherill, who gave much time and work to the perfection of the detail and practice of the operation, and certainly deserved the credit of making it the success it has been. At the present time, every works in this country, but one, uses the Wetherill process. The much lower cost by it and the possibility it gave of profitably working low grade ores have been

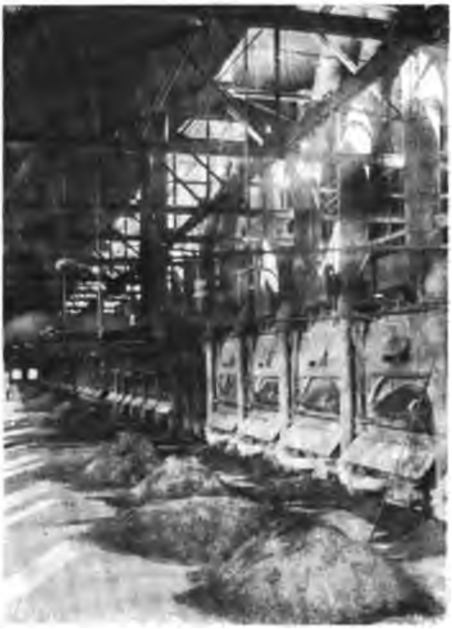


Fig. 16.
Block of zinc oxide furnaces.

the main causes of the tremendous increase in the oxide business of this country, which now produces considerably more than half of the world's supply.

"At first the oxide was collected in large chambers. Later bag-rooms were patented by S. T. Jones, who died shortly after obtaining his patent, and his widow, Martha, sued the company to recover damages. Many other schemes have been proposed and tried since for making and collecting oxide, but so far none have proved as satisfactory as the Wetherill process and the bag-rooms. The improvements have been in detail and have changed the results obtained to a degree that the inventors would not have believed possible. Much larger furnaces are used, more material is treated per square foot of grate, better recoveries are obtained, and the quality of the product is under closer control. These improvements are due to a better understanding of the chemistry of the process, better mechanical arrangements, and closer supervision. There have been no radical changes since Col. Wetherill's day, but he would hardly

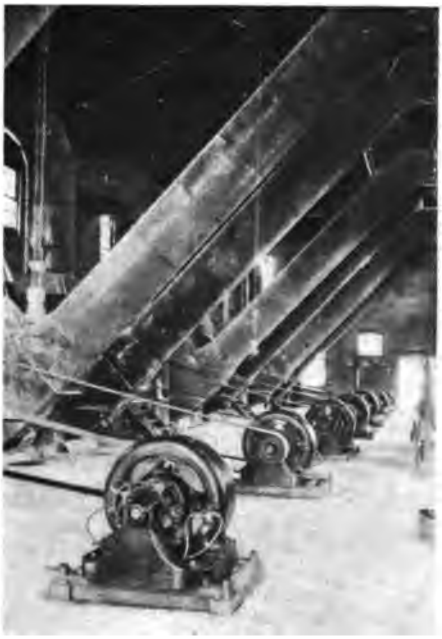


FIG. 17.

Fan room for forcing zinc oxide fume through cooling pipes.

recognize the later plants, as the changes in almost all details have completely altered the general appearance. It is difficult to give credit for these improvements, as almost everyone who has been closely connected with the manufacture has done something, and while the total result of the changes is large, it is impossible to say how much of it is due to any particular one.

"The Florence plant of the New Jersey Zinc Company (of Pennsylvania) is the only one that uses the French process of distilling and burning metallic zinc. The two oxide plants at Palmerton, Pennsylvania, are by far the largest in the world. The older, or West plant, contains 34 blocks of oxide furnaces, and the new, or East plant, 26 blocks. Each block is an independent unit, with its own blower, exhaust fan, and bag-room."

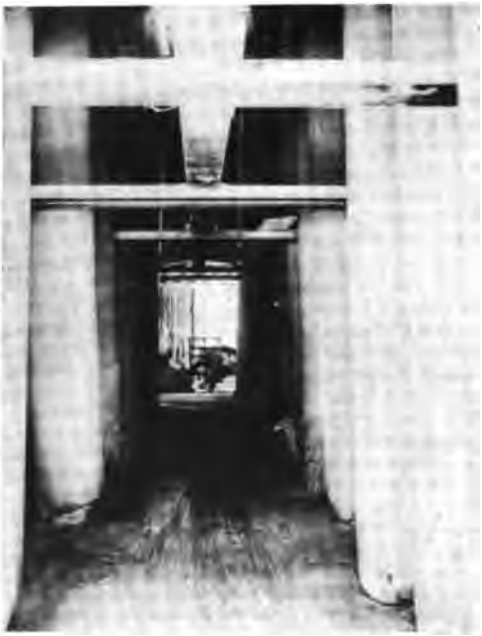


FIG. 18.

Bag room for collecting zinc oxide pigments.

The inability of the producers to make a sufficient quantity of zinc oxide to meet the demands of the last two years has often brought forth inquiries as to why a larger quantity of ore has not been worked up into the oxide. In answering these questions, some statistics regarding zinc ore and spelter are appropriate, as they have a direct bearing on the oxide production. In the first place, it is well to refer to the unusual activity that has been displayed in the metal fabricating industries. The demand that has thus been created for spelter is reflected in the amount of zinc ores mined during 1916 (1,656,000 tons) which produced 672,300 tons of metal; over 220,000 retorts being in operation by the end of the year. The average Joplin price for these ores was $93.00 for high grade and $75.00 for low grade, while the average price of spelter for the year was approximately 13¾ cents for common and at least 7 cents more for high grade. Those who are familiar with the metals market can compare these figures with those prevailing during previous years, and reflect upon the temptation placed before the zinc manufacturer to throw all his available resources into the manufacture of spelter rather than oxide. On the contrary, more lead-free oxide has been made during the past year than in any previous one, and the mines producing ore suitable for this material have largely increased their output, all of which has been utilized for this purpose alone.

Courtesy W. H. Hendricks

FIG. 19.

Zinc oxide bag room at Palmerton, Pa., 805 feet in length.

For the manufacture of lead-free zinc oxide only one type of ore is used. This is a zinc-iron-manganese spinel known as Franklinite, found only in Sussex County, New Jersey. It is associated with Willemite, a yellowish green anhydrous silicate of zinc containing approximately 58 per cent of metal, which is used only for the manufacture of pure spelter. The ore as it is mined is washed, crushed and passed by belt conveyor over a separating table where an electro-magnet removes the Franklinite. In its separated form the Franklinite is black in color and consists usually of from 60 per cent to 80 per cent iron oxide, the balance being a mixture of zinc and manganese oxides. For making zinc oxide, the mineral is first mixed with powdered coal and spread upon a bed of glowing coal on a perforated grate. Air is blown through the charge, burning the coal, with the result that the zinc in the ore is reduced and volatilized. The oxidizing atmosphere in the upper part of the furnace serves to convert the vaporized metal into the oxide. This is drawn, in the form of a white fume, by the aid of huge fans, through large cooling pipes, being finally deposited as a fluffy powder in fabric bags suspended in the bag-rooms at the end of the system. The bags are tapped at the bottom from time to time to remove the oxide, which is then graded for color and packed for shipment. It is interesting to note that one of the bag-rooms referred to above (see Fig. 18) is 805 feet long, 64 feet wide, and 59 feet high. The muslin bags suspended in this room, if sewed together end to end, would cover a distance of thirty miles.

The other zinc-bearing ores are used only for the production of spelter, or, in some instances, for the manufacture of leaded zinc, as indicated below. Of these ores, the most important is zinc blende, or Sphalerite, a very widely distributed mineral. This ore, which varies in color from light yellow to black, consists of the sulphide of zinc, and in the form in which it is delivered to the smelter contains usually from 35 per cent to 65 per cent of metal. the balance consisting largely of iron and manganese oxides. It is found in Missouri, Illinois, Colorado, Wisconsin, Arkansas, Kansas, New Mexico, Arizona, Idaho, Nevada, Utah, Montana, Tennessee, Virginia and Iowa in commercial quantities. Although the bulk of spelter is made from this ore, a considerable amount is still produced from the oxidized ores which include the native carbonate of zinc known as Smithsonite. This ore, by the way, was one of the first employed in zinc smelting in this country, and when fairly pure contains up to 52 per cent of zinc with silica, lime and iron as impurities. It is usually found associated with the hydrous silicate of zinc, known as Calamine, in deposits of considerable extent but relatively small compared to the existing deposits of blende. The Smithsonite ores are found quite widely distributed, the principal deposits being located in Arkansas, Kentucky, Missouri, Wisconsin, Tennessee, New Mexico, Colorado, Arizona, Nevada and Utah. Although it has been used largely for making spelter, it is also used to some extent for the production of leaded zinc.

A substantial amount of metal was used during the past year for making Florence oxide, which is the whitest and lightest grade of zinc oxide produced. It was made by the usual French process of volatilizing pure spelter, burning the vapor, and collecting the fume. Owing to the very high price of the raw material, spelter, there has been no incentive to the manufacturer to make this grade of oxide. Notwithstanding that the profit was nominal, sufficient of it has been made to satisfy all of the demands of the consumers.

Leaded Zinc.—Leaded zinc may be looked upon as a comparatively new pigment that has been introduced with successful results, especially in the manufacture of exterior paints. Probably the first pigment of this type produced on a large scale was that known as zinc lead white, which was made at Canon City, Colorado, by the volatilization and oxidation of mixed lead and zinc ores. During recent years this pigment consisted approximately of equal parts of zinc oxide and lead sulphate. When used in paints, it gave good results on exterior exposure, in nearly every test in which it was used. Its production, however, was discontinued in 1910, and since that time the manufacture of the so-called leaded zincs has been developed on a very large commercial scale, over 23,000 tons having been produced during the past year. The pigment as it is produced commercially, apparently has its lead content in the form of basic lead sulphate. Two samples recently examined by the writer showed, respectively, 3.5 and 13.9 per cent of lead oxide in excess of the amount necessary to combine with the sulphuric anhydride present.

Considerable information regarding the various leaded zinc pigments has already been presented in a circular written for the Educational Bureau by G. B. Heckel, the essential parts of which are given below.

> "Leaded zincs are zinc oxides produced by the American process (that is by direct sublimation and oxidation) from ores

of zinc containing certain percentages of lead ores in association. These ores are comparatively abundant, while lead-free ores are rare. As a consequence it follows that the only grades of American process oxides which promise an expansion adequate to a growing demand are those containing upwards of 10 per cent of basic lead sulphate. These leaded zincs are produced with approximately definite lead contents ranging from 10 to 35 per cent of the basic sulphate. Their color is not as a rule as good as that of the 'horsehead' oxides, but in other respects, considered as paint pigments, they are for many purposes generally regarded as superior. It may be said, in passing, that there is reason to believe that, since the color appears to depend somewhat upon the basicity of the lead sulphate contained, and since the lead oxide present in the basic sulphate appears to enhance the pigment value of the product, improvement of color may involve some sacrifice of pigment quality.

"In none of these leaded oxides is the color sufficiently 'bad' to have any practical importance, excepting in the manufacture of white and very light-tinted decorative paints; and by proper tinting and manipulation, even here the color can be made satisfactory. For all other uses, the difference is negligible in the finished product. From a manufacturing point of view there are several advantages in the use of leaded rather than a pure oxide. The percentage of oil required for grinding and the total volume of 'thinners' required to reduce to painting consistency is less in almost exact ratio to the percentage of lead content; the 'body' of the finished paint is decidedly superior; the durability of the paint would seem to be greater; the cost of the leaded zincs is lower.

"As to the durability of paint made from leaded zincs, the following excerpts from official reports will be sufficiently confirmatory:

"1910. Second Annual Report on Atlantic City Test Fence, Panel No. 39. Zinc lead white: chalking, 'considerable'; checking, 'very slight'; general condition, 'good'. This was the highest rating given to any single pigment paint.

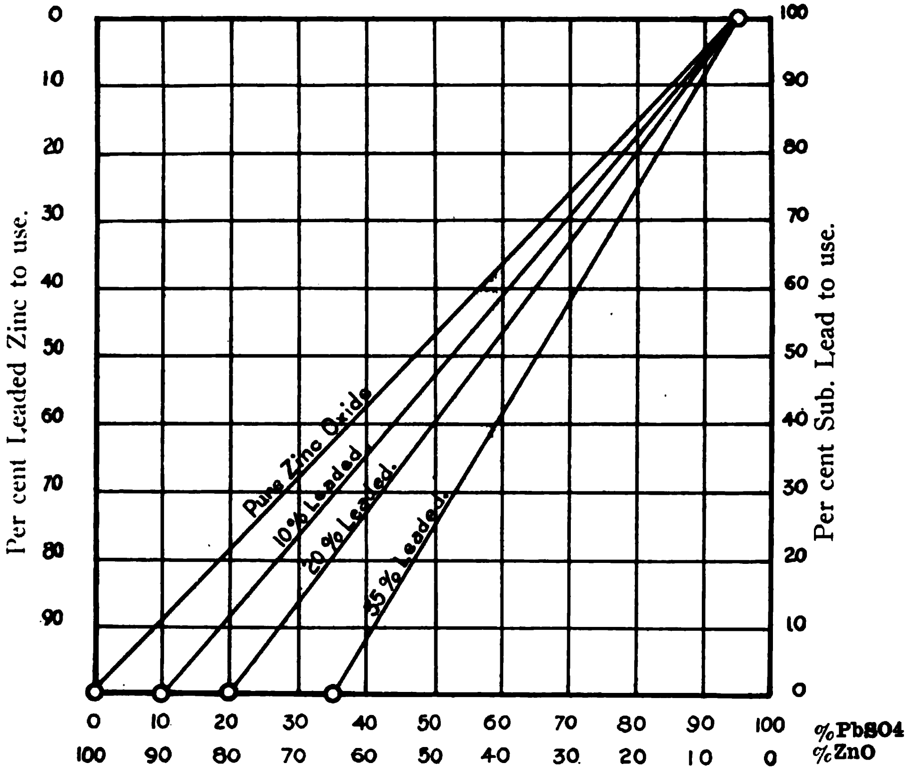
"1913. Report on Inspection of the Tennessee Test Fence. 'Zinc lead, a fume pigment consisting of equal parts of lead sulphate and zinc oxide, gave good results, presenting a surface that was quite free from defects. Leaded zinc * * * was not used as a straight pigment in the tests, but was applied in test No. 5 in combination with basic carbonate white lead (65 per cent leaded zinc, 35 per cent white lead). In such combination it gave good results.'

"1914. Report on Arlington Test Fence, Com. D-1, American Society for Testing Materials. 'Panel No. 107, zinc lead white, shows no checking and surface is very clean.' 'None of the paints composed of a single primary pigment are equal to paints made up of composite pigments, except zinc lead white, which is actually a composite pigment.'

"The following statistics may also prove interesting:

Diagram I.

"Plot Shows Amounts Leaded Zinc and Sublimed Lead to Use for Desired Lead Content of Mix.



"The 35 per cent leaded oxide, when ground with 14 per cent of its weight of linseed oil yields a paste having the same consistency as ordinary white lead in oil. For use as a base for prepared paints the proportion of oil may conveniently be increased to about 22.5 per cent. Such a base may be reduced to good working consistency by the addition of a little less than

50 per cent of its weight of additional oil, thinners and dryer. If rosin in any form appears in the vehicle or the dryer, it should be completely neutralized to prevent reaction with the pigment. It is good practice to use about 10 per cent of turpentine in the vehicle of all leaded zinc paints. Contrary to the practice with basic-carbonate white lead, oils with very low acid number are preferable for leaded zinc paints.

"It is suggested that while objections to the color of these leaded zincs when used for white paint are largely sentimental, it may be greatly improved in practice, by the addition of a very small percentage of blue and also by grinding in refined oil rather than raw oil.

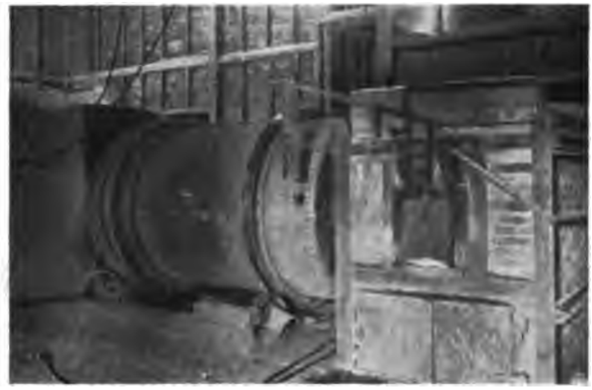
"It is to be noted that in States requiring the formula to be shown on the package, the lead content of all these oxides excepting the lowest (under 5 per cent) must be stated. In all cases where the lead sulphate is actually basic ($Pb3S_2O9$), this is properly given as 'Basic Lead Sulphate.' On the other hand if leaded oxide be used in which the lead content is practically all present as normal lead sulphate ($PbSO4$), the propriety of the designation may be subject to question.

"In practice it is often necessary or desirable to increase the basic lead sulphate content of the formula over that present in the leaded zinc available for use. Since Basic Lead Sulphate (or sublimed lead) as marketed contains about 5 per cent of zinc oxide, calculation of the required proportions of the two pigments required to yield the relative percentages is a rather complicated process.

"The chart (Diagram I) by J. E. Heckel will furnish the required information at a glance.

"The figures to the left indicate the percentages of leaded zinc and those to the right of sublimed lead required to produce the required percentages of ZnO and $PbO4$ indicated at the bottom of the chart. The four diagonal lines represent the several grades of oxide. To find any desired percentages shown in the bottom rows of figures, using any of the oxides shown, follow the perpendicular line to its intersection with the proper diagonal; the required percentages of that oxide and sublimed lead will then be found on the horizontal line to the left and right, respectively. E. g.—Desired percentages 50 each, using a 35 per cent leaded oxide. The 50-50 perpendicular intersects the 35 per cent diagonal at the horizontal line which indicates at the left, 76 per cent leaded zinc, and at the right, 24 per cent sublimed white lead. The desired percentages will, therefore, be obtained by using 76 pounds of the former to 24 pounds of the latter."

Lithopone.—This pigment was apparently first produced by Orr in 1874, and was at once developed in various forms in England and on the Continent. Its use in substantial amounts in America dates back about twenty years, when it was introduced to the oilcloth and linoleum trades to replace white lead, for making printing paints. Later its manufacture was undertaken in New Jersey and Pennsylvania on a comparatively modest scale. In 1914 there were six makers of this pigment in the United States, and the amount produced was relatively small (about 32,000 tons). At the end of 1916 there were nine factories in operation, four of which were making from 40 to 65 tons a day, the others averaging or contemplating a daily output of 15 to 20 tons. It is probable, however, that the total amount produced during 1916 was not over 75,000 tons. The indications are, however, that during the year 1917 there will be a production of substantially 100,000 tons. Among the factors contributing to the rise in price of this product during the last two years may be mentioned the stoppage of the import of German barytes, thus requiring the use of the American grade which could not previously be used, solely on account of the high freight rates to the points of pigment manufacture. The high prices of spelter and sulphuric acid, both of which are required in large amounts for lithopone manufacture, also greatly increased the cost of production.

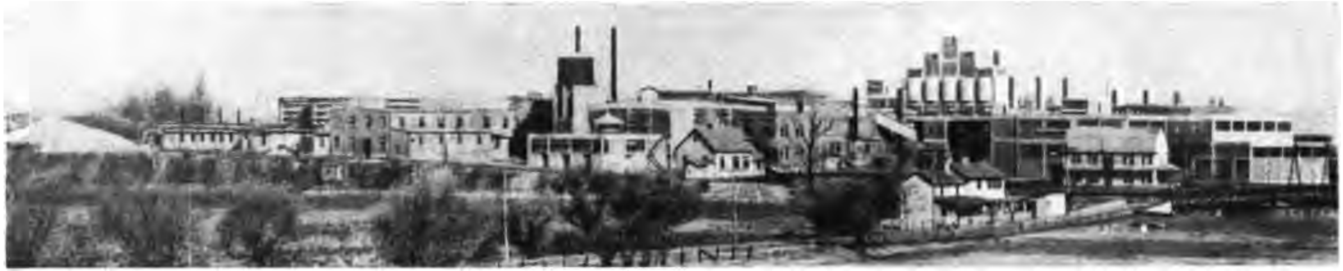


Courtesy H. V. Berg

FIG. 20.

Rotary furnace for roasting barytes and coal to produce barium sulfide.

While it is probable that the rapid growth in the production of



Courtesy H. V. Berg

FIG. 21.

View of one large plant devoted solely to production of lithopone pigments.

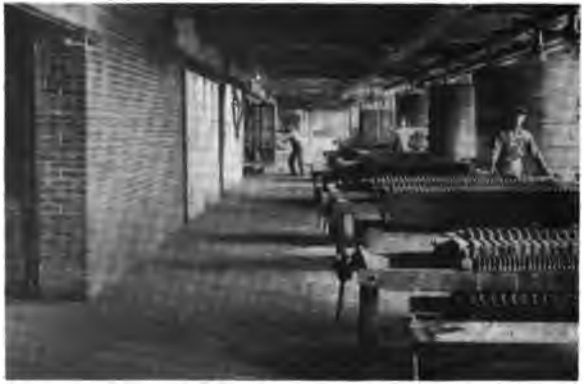
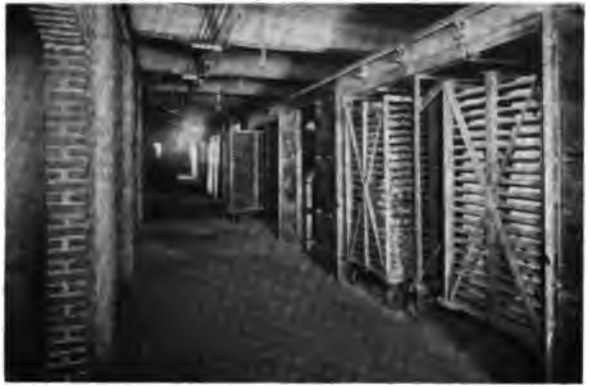


FIG. 22.

Filter presses used for extracting water from precipitated pigments.

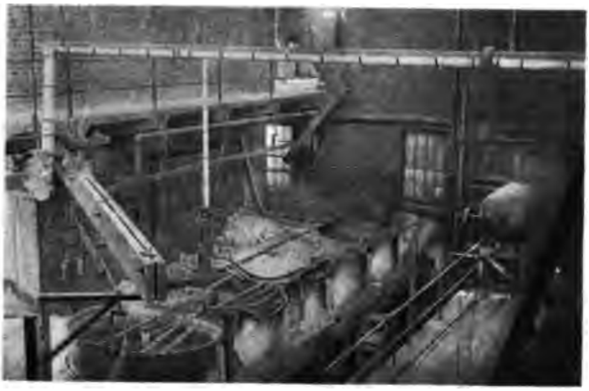


Courtesy L. P. Nemzek

FIG. 23.

View of racks and drying ovens such as are used for drying precipitated pigments.

lithopone in America should be attributed to a great extent to the modern desire for interior flat wall paints of the lithopone type, its use has also been increased by the demands for it in various industries. For instance, large amounts are used in the manufacture of linoleum, oilcloth and shadecloth, and, in fact, wherever a pigment of great whiteness and hiding power is required. The opacity of this pigment is commented upon, page 45, under Opaque Adsorption Pigments.



Courtesy H. V. Berg FIG. 24.

Tanks for extracting barium sulphide used in lithopone production.

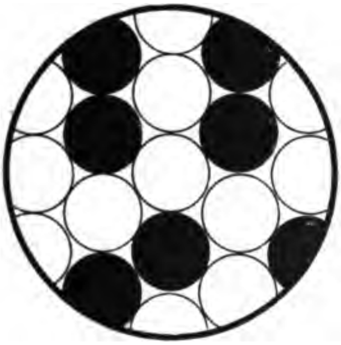


FIG. 25.

Diagrammatic view of mixture of transparent and opaque pigments.

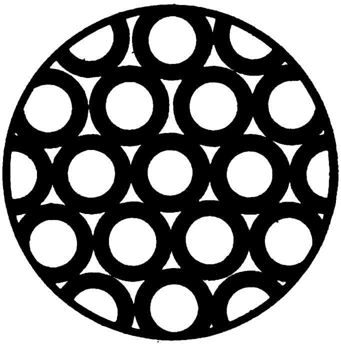


FIG. 26.

Diagrammatic view of precipitated pigment composed of transparent pigment coated with opaque pigment. Better hiding power is obtained from a precipitated pigment than from a mere mechanical mixture of the same pigments.

A number of American and foreign manufactured lithopones, used by the writer in exposure tests, were analyzed and the following results obtained, which show the composition of the average grade used in paints:

	Composition.		
No.	ZnS.	$BaSO_4$.	ZnO.
A	27.80	70.44	1.26
B	26.41	71.06	2.48
C	26.48	71.18	2.12
D	28.42	70.22	.70
E	27.10	71.18	1.20
F	27.97	71.02	.54
G	26.72	70.42	2.36
H	27.87	70.40	.82
I	27.90	70.30	.94
J	30.27	69.68	.22
K	29.09	70.10	1.30
L	26.94	72.36	.50
M	27.61	70.50	1.04
N	26.27	72.54	.76

While lithopone is very satisfactory for use in interior paints, it has not proved durable on exterior exposure. When exposed out-of-doors, it rapidly darkens and chalks away, leaving a rough film of little protective value. Tests of several years' duration have, however, shown that better results are obtained when lithopone is combined with certain other pigments. The formulas used in these tests are shown in Bulletins 34 and 35 of the Scientific Section, Paint Manufacturers' Association of the United States. When these paints are tinted, much better results are obtained than in white. For painting cement surfaces, certain mixtures containing lithopone as a component part of the paint pigment composition have also indicated good results.*

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* Bulletin 53, Paint M'f'rs Ass'n of the U. S.

CHAPTER III.

PHYSICAL CHARACTERISTICS OF PIGMENTS AND PAINTS.

(*Colloidal Condition of Paints.*)

HIDING POWER OF PIGMENTS.

The opacity or hiding power (covering ability) of a paint pigment depends upon its fineness, refractive index, and oil absorption. These physical properties are responsible for the fact that a coat of white lead in oil hides a dark surface better than a coat of silica in oil.

Fineness.—Paint pigments, if produced in sufficiently large-size particles, would be more or less transparent like a lump of glass, since all such products allow the light to be transmitted in varying amounts. If any one of them, however, is broken down and powdered, the finely divided particles reflect the light in all directions and only a small amount of light is transmitted; the powdered substance thus appears opaque. Therefore, it may be stated that *the opacity of pigments increases with fineness of division.* With some pigments, however (produced by the fume process), there may be a point beyond which increasing fineness may result in a lowering of opacity.

Refraction.—The refractive index of a pigment determines the amount of light that will be transmitted by it—the higher the refractive index, the greater the reflection and consequent hiding power. A layer of white lead will reflect more light than a layer of finely ground silica, since the refractive index of the lead is higher than the refractive index of silica. When either of these pigments are ground in water, the same phenomenon holds true, but both are less opaque than in dry form because water has a higher refractive index than air. *As the refractive index of the vehicle approaches that of the pigment, opacity diminishes,* an optical condition being produced by the film around the particles, that allows the passage of light, thus decreasing the reflection. When turpentine is used as a binding medium, the pigments show the same relative differences in hiding power, but both are less opaque than when in water, since turpentine is more highly refractive than water. When linseed oil is used as a medium, still less opacity is shown by the resulting paints, as linseed oil has a greater refractive index than turpentine. The resulting silica paint will now be practically transparent, since the refractive index of the medium is substantially the same as that of the pigment. The lead paint, however, will still be opaque, since white lead has a refractive index greater than that of the oil.

Oil Absorption. — *Opacity increases inversely with the amount of oil absorbed by the pigment.* This is shown by comparing the hiding power of lead and zinc whites. These pigments have substantially the same refractive index and theoretically should hide equally. As a matter of fact, however, a workable lead paint has greater hiding power, since it may be produced by grinding 70 parts of lead in 30 parts of oil, while a workable zinc paint will contain 50 parts of zinc and 50 parts of oil. More light will pass through a film of the zinc paint than through the lead paint, on account of the greater quantity of oil present in the former. This accounts for the difference in the hiding power of the two paints. The preponderance of oil in the zinc paint, however, accounts for the much greater durability of those paints which contain zinc oxide in combination with lead pigments, since. abundance of oil is recognized as a necessity in exterior paints.

It is apparent from the above considerations that the hiding power of a white pigment is measurable by determining its physical characteristics. Various methods for determining fineness and oil absorption have been in use, but no method has apparently been adopted for determining the refractive index of pigments. It occurred to the writer that some application of the petrographic microscope might be made for this purpose. A series of pigments were therefore prepared and submitted to test, the readings being made by Dr. Frederick E. Wright, of the Carnegie Geophysical Laboratory of Washington. Small particles of the pigment under observation were rubbed up with media of known refractive indices, covered with glass, and submitted to examination. Some of the readings are shown below:

Quartz silica	1.55	Basic carbonate—white lead	2.0
Barium sulphate	1.6	Basic sulphate—white lead	2.0
Zinc oxide	1.9+	Zinc sulphide	2.2 to 2.37

OPAQUE ADSORPTION PIGMENTS.

One of the most interesting pigments examined was lithopone. Difficulty was experienced in getting an exact reading, as it consists of a submicroscopic mixture of aggregated particles. It is possible that the average refractive index might be considered as being between 1.9 and 2.0. This pigment is prepared by the resulting interaction of chemically equivalent amounts of zinc sulphate and barium sulphide solutions. The precipitated pigment is calcined, quenched, washed and dried. It consists of approximately 70 per cent barium sulphate and 30 per cent zinc sulphide. When barium sulphate, which has a refractive index of 1.6, and zinc sulphide, which has a refractive index of 2.2 to 2.4, are *mixed* in the above named proportions, a pigment is produced which is deficient in hiding power. It is apparent, therefore, that the precipitation process of preparing these pigments produces some physical change which is of great importance. It is the writer's opinion that the effect is due to absorption of the zinc sulphide by the barium sulphate particles. Microscopial examination indicates that each particle of finely divided barium sulphate is coated over by adsorbed particles of opaque zinc sulphide. Experiments have been made with varying strengths of barium sulphate and zinc sulphide liquors in varying amounts, to determine whether it would be possible to produce even more opaque types of lithopone by increasing the amount of the zinc sulphide present. When lithopones are made containing as high as 50 per cent zinc sulphide, the hiding power has not been found substantially greater than that of lithopone, which contains from 28 per cent to 38 per cent of zinc sulphide. Below 28 per cent of zinc sulphide, the hiding power of the pigment decreases. It is, therefore, between the limits of 28 per cent and 38 per cent zinc sulphide that the greatest hiding powers are obtained, and the increased hiding power of lithopone containing 38 per cent is hardly greater than that shown by those containing the theoretical equivalent of 30 per cent. Rapidity of precipitation, strength of solution, and temperature control are factors which also aid in the production of fine-grained particles that give the pigment great opacity.

The phenomenon of surface adsorption shown by certain lake bases in the presence of organic coloring matters is also interesting, and explains why the highly colloidal pigments are often preferred for this purpose. A measure of the degree of dispersion of pigments might be based on their color adsorption values.

SUSPENSOID PIGMENTS.

The adhesive properties and cementing values of paint pigments apparently increase with approach to colloidal form. That all paint pigments are to some extent colloidal, is the assumption of the writer as the result of some recent tests. These were first suggested by some previous experiments in which a number of white pigments were ground in clear linseed oil. After standing for a year, the oil upon the surface of the settled paints was examined and found to be much higher in ash than the original oil. This condition could easily be accounted for in the case of the lead and zinc paints by the presence of dissolved metallic linoleates formed by reaction between the pigments and the free fatty acid of the oil. No explanation, however, was offered as to the cause of the high ash in those paints made of silica, barium sulphate and other pigments which it was thought could exert no chemical effect upon the vehicle. A sample of the oil from one of the inert pigments (blanc fixé), after standing in a bottle for a further aging period, became viscous and thick, later on developing a peculiar cloudiness. Examination showed that the pigment had probably been held in colloidal suspension and previous to its precipitation had effected a change in the oil that had caused the gelatinous condition. As a result of these observations, the writer prepared a series of paints by grinding in a clear linseed oil a number of standard white pigments, including basic carbonate- and basic sulphate-white lead, zinc oxide, lithopone, and china clay. After settling for a period of two weeks, the clear oil was removed from each paint. The oils were examined under the ultramicroscope by Dr. E. C. E. Lord, of the U. S. Office of Public Roads, and the writer. Particles were visible but apparently in a quiescent state. This condition was undoubtedly due to the viscosity of the oil media which exerted a cohesive force upon the particles, binding them together in aggregates and thus impeding their motion so that the Brownian movement was not observable. These liquids, however, after dilution with 4 volumes of redistilled 90° benzol (disperse free) were again examined. The viscosity of the media thus being reduced, great rapidity of motion of the particles was shown. This Brownian movement was observed in every liquid and indicated that all of the above pigments may contain particles that act as suspensoids in oil. A sample of the original oil used in making the paint was also examined and although Brownian movement was observed therein, the number of particles present was not comparable to those shown by the oils removed from the paints. The particles present in the original oil were probably due to the "foots" present, regarding which reference is made below.

For the sake of convenience, the writer has given the name of "Linosols" to pigment suspensoids, since paint pigments are almost universally used in conjunction with linseed oil. When a condition is produced by these pigments, whereby the oil assumes the state of a gel, as in the case of the blanc fixé pigment mentioned above, the product of reaction might be called a "Linogel." The precipitation of the blanc fixé which was first visible as a cloudiness in the oil might possibly have been caused by absorption of oxygen by the oil, and would then be comparable to the precipitation of silica when carbon dioxide is absorbed by a sol of hydrated silicic acid. The term "Linoxygel" might, therefore, be more acceptable for such a product.

Experiments were then made with the same series of pigments ground in various oils, including a heavy bodied linseed oil of very high viscosity. In the latter, separation of the pigment from the oil, even after standing for two months, was only partial. After the paints were diluted with 4 volumes of benzol, only the coarser particles subsided, the liquid above remaining cloudy and suggestive of a true colloidal condition—the subdivided particles no longer showing any tendency to settle. Even after standing five weeks, the same cloudy condition was observed. It was apparently impossible to clarify the turbid liquid by sedimentation, even with the aid of a high-speed centrifuge. Attempts were then made to precipitate the Linosols. It was found that by mixing two of the cloudy paints (zinc oxide and silica), a fairly clear liquid could be produced. The explanation of this phenomenon might be that the pigments being oppositely charged had neutralized each other and thus disturbed the disperse phase, resulting in precipitation.

COLLOIDAL COLOR PIGMENTS.

In order to study the condition of finely divided colored pigments, several were selected, including Prussian Blue, Chrome Green, Chome Yellow, Ultramarine Blue, Lampblack, and Paranitraniline Red. These were ground in the same type of oil that was used with the white pigments, and treated in the same fashion. The clear liquid shown after settling was diluted with 4 volumes of benzol (disperse free) and examined. It is of interest to record the fact that the oil obtained from the settled Para Red pigment was only slightly colored, but when benzol was added, it became a bright, clear red. It is probable that part of the pigment present as a suspensoid was brought into actual solution by the solvent power of the benzol upon the organic coloring matter present in the pigment, thus accounting for the increase in color. When the liquids were examined under the ultramicroscope, Brownian movement was exhibited by each, the green and blue being most active and apparently containing many times the number of particles present in the others. Comparing the blue roughly with a counted solution of colloidal asphalt, it is probable that 1 cc. of the liquid contained over a hundred million particles.

Many of the particles or aggregates in the oil from the Chrome Green were colored crimson, orange, green, and blue.

The colors were apparently permanent and did not change as would be the case if due to refraction. Since it is supposed that ultramicroscopic particles simply reflect light and therefore do not show colors, the above result is interesting and should warrant some extended work on the subject.

PREFERENTIAL ADSORPTION EFFECTS.

The effect shown by carbon black is worthy of study. This pigment is supposed to be one of the most inert to linseed oil. It is probable, however, that it is really one of the most active in some ways. The great surface which its particles present, on account of their extreme fineness of division, probably gives to it very high adsorptive properties. The purest pigment obtainable by burning oil may be free of other solids and yet, according to F. P. Ingalls,* contain only from 80 to 90 per cent of carbon, the balance consisting of carbon monoxide, carbon dioxide, hydrocarbon compounds, nitrogen, oxygen, and water, all of which have been adsorbed by the carbon particles during the process of manufacture. That these substances are firmly locked to the particles is apparent, since vacuum treatment of the pigment fails to remove them. When ground in oil, however, the writer believes that the gas is removed from the pigment and the oil is adsorbed in place thereof by a preferential adsorption action of the pigment. Clifford Richardson has shown, for instance, that asphalt particles have the power of adsorbing some of the heavier constituents of a liquid by preferential adsorption. The present writer has similarly noticed that some finely divided pigments may absorb the heavier constituents of an oil medium. This may be shown by dissolving a very heavy bodied linseed oil in benzine and grinding it with lithopone. After a period of time, a reaction will be effected, whereby the oil is adsorbed by the settled pigment, leaving a clear, oil-free benzine floating on top. Very strongly oxidized and bodied oils may even show precipitation upon standing after being mixed simply with benzine. It is a question, therefore, whether any true solution of the oil has originally taken place. It is very likely that the apparent miscibility of the benzine is due in this instance to a sponge-like process of imbibition which might be compared to the absorption of benzol by rubber, or the swelling of gelatin in water (these effects, however, are illustrative of emulsoids). The preference shown by pigment particles for various liquids is aptly illustrated in the manufacture of pulp lead. The white lead, which contains a large amount of moisture, if agitated with linseed oil will immediately unite with the oil, and the water will be thrown out, floating on the surface of the paste paint. Other pigments and liquids may show a similar reaction. When zinc oxide or lithopone, for instance, are ground in alcohol and subsequently agitated with linseed oil, the oil will immediately unite with the pigments and the alcohol will be found floating on the surface of the paste. It is probable that these reactions have been made possible by a lowering of surface tension by the introduction of the oil.

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*Private communication.

SUSPENSOIDS IN OIL AND VARNISH.

The "foots" present in linseed oil offers another example of what might be termed a "Linosol." When freshly crushed from the flaxseed, the oil will be apparently clear. If heated to 100° C., it will become cloudy and a large precipitate will form. This is referred to as "foots" and consists of mineral matter—lime, silica, phosphoric acid, etc.—admixed with albuminous matter. The mineral matter is present in the raw oil as a suspensoid* and is agglomerated and precipitated when the albumen is coagulated by the heat. The aging of oil may accomplish a somewhat similar effect, but sufficient tankage space is not always available to the crusher, and, therefore the raw oil is often marketed immediately after it has been produced. In the writer's opinion, such oil is not fit for use in high-grade paints, and the grinder should demand a better product. If the crusher should heat the raw oil to 100° C. and then centrifuge it, this method might take the place of tanking and would, at the same time, accomplish the destruction of fat-splitting enzymes* which might be present in the oil.

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*"Refining Vegetable and Animal Oils," Chas. Baskerville, J. Franklin Inst., June, 1916.

Varnish constitutes another organic product that may contain mineral suspensoids. Tanking of clear, newly made varnish always results in a slow precipitation of "foots." Centrifugal force will bring about the result more rapidly. It is gratifying to note that the centrifuge has become a part of the equipment of every modern varnish plant, and its use in this industry is bound to be more extended in the future. E. E. Ayres† has recently commented upon the clarification of pyroxylin varnishes by centrifugal action. and has mentioned the remarkable effect of a precipitant such as tricalcium phosphate. Similarly it is probable that the addition of certain mineral matter to freshly made varnishes, just previous to centrifuging, may effect more rapid and permanent clarification.

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*See "Changes Occurring in Oils and Paste Paints, Due to Autohydrolysis of the Glycerides," p. 286.

† "The Application of Centrifugal Force to Suspensions and Emulsions," E. E. Ayres, J. Ind. & Engrg. Chem., June, 1916, p. 676.

CHAPTER IV.

TESTS OF LITHOPONE.

The difference in quality exhibited by various grades of lithopone makes it desirable for the consumer to conduct tests to determine what type is best suited for the manufacture of paints. Methods of testing the chemical and physical properties of this pigment are given herewith. There is also given in chart form the preliminary results of a recent series of tests conducted by the writer at Washington on several grades of lithopone obtained in the open market. These tests include exposure tests on large-sized panels which were given three coats of paints prepared from lithopone and linseed oil.

Physical Tests on Lithopone.

Color.—The color of the dry pigment should be compared with a standard sample of pure dry zinc oxide and a standard sample of lithopone that has been kept in a colored glass jar protected from light. Portions of these samples should then be ground in light-colored linseed oil and again compared for whiteness.

Opacity.—The relative opacity or "dense" character of the samples may be determined by making small batches of paste paints with mortar and pestle. To 25 grams of lithopone add 2 grams of 98% red oxide of iron. Use about 10 grams of raw linseed oil (pale) for grinding. Brush out a sample of the paint upon a strip of glass in comparison with others prepared in the same manner. The most "dense" grade of lithopone will give the lightest tint.

Fineness.—For determining the fineness and freedom from large particles, place 100 grams of lithopone in a 350-mesh screen.* Wash sample through by holding screen under tap of running water. Brush particles back and forth over surface of the screen until the fine particles have all been washed through. Dry and weigh the residue and compare with results on other samples.

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*As recommended by C. D. Holley in "Rapid Test for Fineness of Pigments." Screen made by Multi-Metal Separating Screen Co., 68 East 131st street, New York City.

Sun Test.—In a porcelain mortar, grind 25 grams of lithopone and about 10 grams of water to a smooth paste. Brush out sample on a glass plate and place in sun. Make comparison with other samples. On a cloudy day, in absence of sunlight, use a Cooper-Hewitt mercury vapor lamp or an arc light rich in ultraviolet rays.

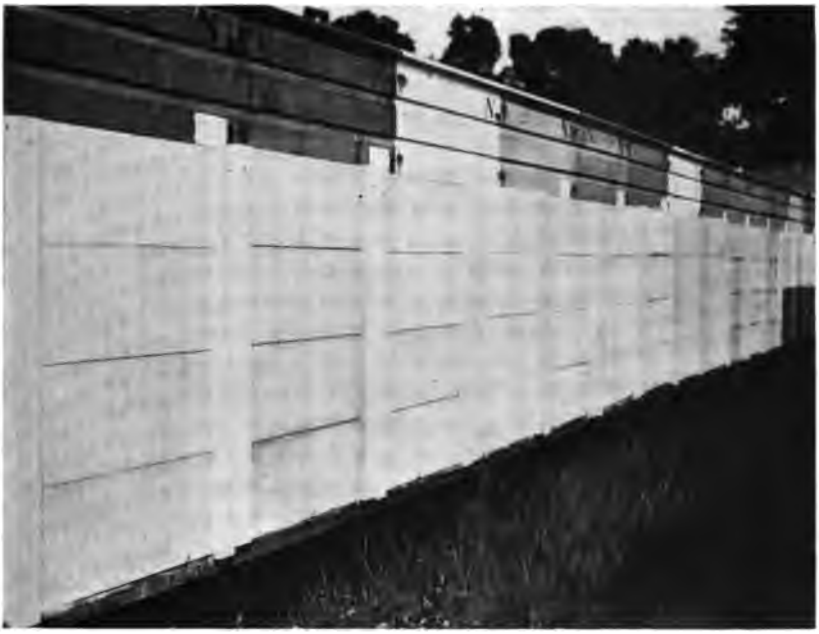

Fig. 27.
View of Lithopone Tests.

Grinding Tests.—Prepare a small batch of lithopone paste by grinding 20 lbs. of lithopone in 10 lbs. of raw linseed oil (pale). The bulking value or pounds per gallon can then be determined in comparison with other samples. The body or viscosity of the paint may also be observed. The paste prepared in this manner may be used as the basis of practical paint tests which may be made by further thinning the paste with sufficient oil to bring it to painting consistency, adding drier and turpentine if necessary. These tests should all be made in comparison with other brands. The resistance of the oil-lithopone paint to the action of the sun may be determined in the manner described above for water-lithopone paste.

Analysis of Lithopone.[*]

Insoluble and Total Zinc.—Take 1 g. of the sample in a 200-cc. beaker, add 10 cc. of concentrated HCl, mix, and add in small portions about 1 g. of $KClO_3$; then heat on the steam bath until about half of the liquid is evaporated. Dilute with H_2O, add 5 cc. of dilute H_2SO_4 (1:10); boil, let settle, filter, wash, ignite, cool, and weigh the insoluble, which should be only $BaSO_4$; make a qualitative examination for alumina and silica. The insoluble should be examined under the microscope for the presence of natural crystalline barytes. Sample may also be examined direct. Make filtrate from insoluble alkaline with NH_4OH, acid with HCl, add 3 cc. of concentrated HCl, dilute to about 250 cc. with H_2O, heat nearly to boiling, and titrate with $K_4Fe(CN)_6$ solution as under zinc oxide. Calculate to Zn.[†]

Zinc Oxide.—Treat a 4-g. sample of the lithopone for 4 hours with 200 cc. of 1 per cent acetic acid at room temperature, stirring occasionally. Filter by suction on a double filter paper and wash with cold water; add to the clear filtrate 13 cc. of concentrated NH_4OH, neutralize with HCl, and then add 3 cc. of concentrated HCl in excess; heat to boiling and titrate with $K_4Fe(CN)_6$, using uranium-acetate solution as an outside indicator. Calculate to ZnO. Calculate this result to Zn, subtract from total Zn, and calculate the difference to ZnS. (Any $ZnCO_3$ or $ZnSO_4$ is included in the ZnO.)

Zinc Sulphide.—Place 0.5 g. of pigment in evolution flask with about 10 g. of "feathered" or mossy zinc, add 50 cc. of water; insert the stopper carrying a separatory funnel and an exit tube. Run in 50 cc. of concentrated HCl from the funnel, having previously connected the exit tube to two absorption flasks in series; first flask contains 100 cc. of alkaline lead-nitrate solution, second flask 50 cc. of same as a safety device. After all of the acid has run into the evolution flask, heat slowly, finally boiling until the first appearance of steam in the first absorption flask; disconnect, let the lead sulphide settle, filter, wash with cold water, then with hot water till neutral to litmus paper and washings give no test for lead. The PbS precipitate is dissolved in hot, dilute HNO_3, evaporated to fumes with H_2SO_4, and finally weighed as $PbSO_4$. Calculate PbS or $PbSO_4$ to ZnS.

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[*] Tentative method of A. S. T. M.

[†] The regular gravimetric method for estimating zinc may be employed by those who prefer it to the volumetric method.—H. A. G.

The alkaline lead solution is made as follows: Into 100 cc. of KOH solution (56 g. in 140 cc. of H_2O) pour a saturated solution of lead nitrate (250 g. in 500 cc. of H_2O) until the precipitate ceases to redissolve, stirring constantly while mixing. About 3 volumes of the lead solution will be required for one of the alkali.

Instead of absorbing the evolved H_2S in alkaline lead-nitrate solution, a solution of 8 g. of cadmium chloride in 250 cc. of water and 150 cc. of NH_4OH (sp. gr. 0.90) may be used. The CdS precipitate may be filtered on a weighed Gooch, washed with water containing a little NH_4OH, dried at 100° C., and weighed. Calculate to ZnS. It is better to filter the CdS on a small filter and wash as above, then place filter and precipitate in a beaker and dissolve in HCl and $KClO_3$ (keeping at room temperature at first); filter out any paper pulp or insoluble matter; make filtrate alkaline with NH_4OH, then just acid with HCl, heat to boiling, and precipitate with $BaCl_2$ in usual manner. Filter, wash, ignite, and weigh $BaSO_4$. Calculate to ZnS.

For very rapid work the contents of the absorption flask, after all H_2S has been absorbed, may be washed into a vessel with *cold* water and diluted to about one liter, acidified with concentrated HCl and titrated with standard iodine solution, using starch indicator. (The precipitate should be completely dissolved.) The iodine solution is prepared by dissolving about 12.7 g. of pure resublimed iodine and 18 g. of KI in a little water and then diluting to one liter.

TABLE 4.—*Tests on Lithopone.*

					TESTS ON DRY PIGMENT		TESTS IN OIL**				
Panel	Designation	Composition.			Color	Darkening Test in Water Paste	Bulk Wt. per gal. (pounds)	Consistency	Average Spreading Rate. One Coat	Darkening at end of 24 hrs. Exposure	Darkening at end of three Months Exposure
		ZnS	BaSO4	ZnO							
A	INT	27.80	70.44	1.26	Very white	Slight	16.3	Heavy	865	Slight	Considerable
B	13	26.41	71.06	2.48	Very white	None	15.3	Heavy	843	None	Considerable
C	14	26.48	71.18	2.12	White	None	16.3	Very heavy	655	None	Some
D	O.	28.42	70.22	.70	Very white	Very slight	16.6	Medium	700	None	Only at edge of panels
E	W. R.	27.10	71.18	1.20	Very white	Very slight	16.7	Thin	780	None	Only at edge of panels
F	D. G.	27.97	71.02	.54	Very white	None	16.7	Thin	745	None	Considerable
G	a	26.72	70.42	2.36	Off color	None	16.6	Heavy	960	Considerable	Considerable
H	b	27.87	70.40	.82	Very white	Badly darkened	16.8	Medium	755	None	Only at edge of panels
I	c	27.90	70.30	.94	Very white	Badly darkened	16.8	Medium	755	None	Only at edge of panels
J	R	30.27	69.68	.22	White	Badly darkened	17.1	Thin	980	Considerable	Considerable
K	G	29.09	70.10	1.30	Very white	Badly darkened	17.0	Medium	950	Considerable	Very dark
L	BN	26.94	72.36	.50	Very white	Badly darkened	17.0	Heavy	900	Considerable	Very dark
M	N	27.61	70.50	1.04	Very white	None	16.6	Heavy	885	None	Considerable
N	IMP	26.27	72.54	.76	Very white	None	16.4	Heavy	960	None	Some
O*		Lithopone 50, Zinc Oxide 50.							920	None	None
P*		Lithopone 40, Zinc Oxide 40, Whiting 20.							890	None	None
Q*		Lithopone 40 Sublimed White Lead 30, Corroded White Lead 30.							865	None	None

* Mixed paint prepared from M lithopone. Made in white and yellow.

** The paints were prepared containing 70 parts lithopone and 30 parts of pure raw linseed oil. For application to the panels, the paints were thinned to contain 60 parts pigment and 40 parts vehicle.

NOTE: Paints O and P gave the best results at the end of eighteen months. The other paints darkened and chalked excessively. For the results of long time exposure tests on lithopone exterior paints see complete report on pages 174-181, "Paint Technology and Tests," by H. A. Gardner—McGraw-Hill Book Co., publishers.

CHAPTER V.

WASHINGTON PAINT OIL TESTS.

The high price attained by linseed oil at various times, together with the uncertainty of the supply, has led many investigators into the field of research, with a view of discovering some mixture of other oils to partly replace linseed oil. Many valuable contributions to oil technology have resulted, but the makers and users of paints have wisely demanded specific and authoritative information as to the practical value of proposed mixtures before adopting them. The writer has made several interesting exposure tests with wooden panels painted with paints made up with various percentages of paint

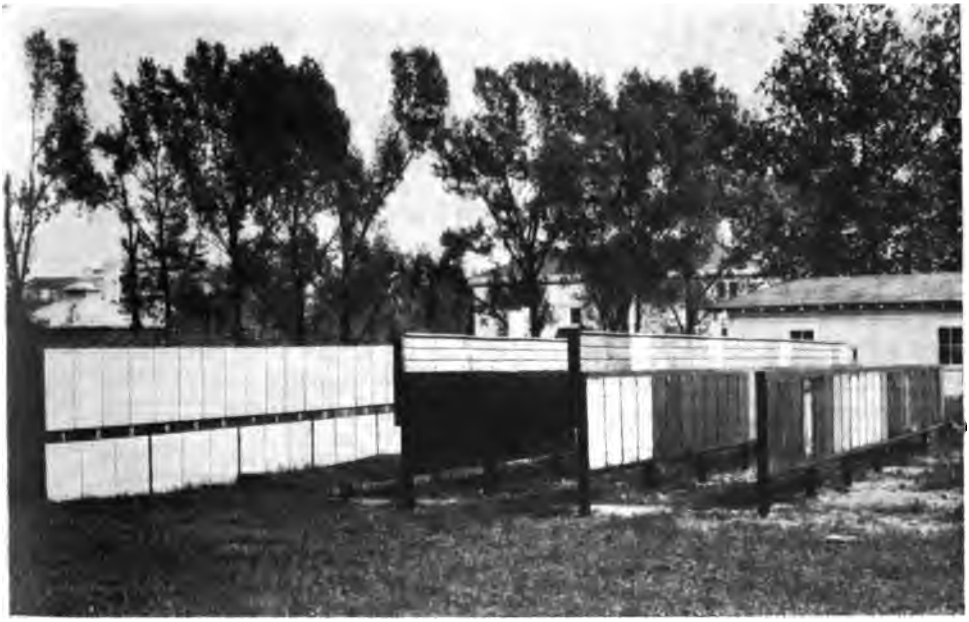

FIG. 28.

Test Frames at Washington on Grounds of the Institute of Industrial Research, Showing Several of the Paint Exposure Tests Which are Being Conducted.

oils. The first series of tests made were at Nashville, Tenn.* The second series, which is probably the most comprehensive, were made in May, 1911, on forty-eight white-pine panels which were placed upon a test frame on the grounds of the laboratory at Washington. They were painted with a standard white pigment formula, reduced with a different oil formula for every panel. White-pine panels were selected for the test on account of the good painting surface which this type of lumber presents; the grade selected was free from knots or pitch pockets—defects which often ruin a paint test. Each panel was constructed of four tongued-and-grooved planed boards, 22 ins. long, 1 in. thick, and 9 ins. wide. The boards were leaded together and capped at the sides with weather strips, making the finished panels about 2 ft. wide and 3 ft. high. The fence upon which the panels were placed was constructed of 4-in. squared yellow pine with open framework, allowing the panels a resting place, upon which they were finally secured with sherardized screws.

Before erecting the panels, they were carefully painted in a paint laboratory especially fitted out for the tests. The work was done during the months of April and May, the temperature averaging from 60° to 90° F. This precaution was taken in order that the paint in each case might become thoroughly dry and hard before exposure, so that there would be no accumulation of dust during the drying period.

The viscous nature of several of the oils tested precluded the possibility of grinding each oil formula with the white pigment base selected. Great heating of the paint mills and a paste of insufficient fineness was the result of an early attempt at this method. It was decided, therefore, to grind the standard pigment formula to a thick paste in the minimum amount of raw linseed oil. Subsequently a weighed amount of the white pigment base was thinned with the oil formula to be tested, to a condition suitable for third-coat work. When making the reductions with oil mixtures, an allowance was made for the amount of linseed oil already contained in the ground white pigment base.

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* See "Paint Technology and Tests," McGraw-Hill Book Co.

During the application of the first coat an equal amount of turpentine was added to each formula, in the proportion of one-half pint to a gallon of paint. In the application of the second coat there was added to each formula a like amount of an equal mixture of turpentine and the oil formula under test. The third coat was applied without the addition of thinners of any kind. Driers were not used in the primary paintings.

The systematic methods which are necessary when making paint tests were carefully followed. A standard weighed amount of white pigment paste was placed in a clean paint cup and thinned to the proper consistency with a weighed amount of the oil under test. Proper reductions were made, as stated above. Weighings of the paint, cup, and brush were made before and after painting each panel, in order to determine the quantity of paint used and the spreading power. A period of fifteen days was allowed between the application of successive coats, in order to give each formula sufficient time to dry thoroughly. After initial drying the panels were exposed to the weather between each coat so that thoroughly oxidized films would be obtained. The backs and edges of each panel were painted with two coats of the paint used on the face of the panel, so as to prevent the admission of moisture. After erection, the panels were numbered with aluminum figures pressed into the surface.

During the painting of the panels considerable information was obtained, of which the following is a brief résumé:

The hiding power of a paint is one of its most important requisites. It was found in the tests that some oils had the effect of lessening, while others had the effect of increasing the hiding power of the standard pigment formula. This may be due in part to the varying refractive indices of the oils used, as well as to the difference in the quantity of oil required in each test.* Some oils were very viscous, while others were very mobile.

The stiff working of heavy-bodied, blown or heat-oxidized oils, produced films which in some cases gave a very glossy surface, even on the priming coat. Some of these produced surfaces resembling varnished work. The treated tung oil paints worked rather hard, but produced very smooth films. The rosin oil paints became slightly lumpy on standing, but worked out to a smooth finish somewhat yellow in color. The marine animal oils, especially the menhaden oil mixtures, dried to a film slightly flatter than straight linseed oil. Any odor which was present in the paints made from the animal oils seemed to disappear a few hours after application. The cotton seed and corn oil mixtures made the slowest drying paints, but at the end of the second week of the drying period they set up rapidly to firm films. Soya bean and perilla oils behaved like straight linseed oil, the former being a little slower and the latter slightly more rapid in drying properties. The perilla oil was made from one of the first importations into this country, and was dark in appearance. It made, however, a very easy-working and hard-drying paint.

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*See "Physical Characteristics of Pigment and Paints," p. 43.

The oils used in the tests were obtained from reliable sources. After they were received they were carefully analyzed. The results of the analyses appear in Table 5.

TABLE 5.

Original Analyses of Oils Used in the Vehicle Tests.

	Specific Gravity.	Saponification No.	Iodine No.	Acid No.
Raw Linseed Oil	0.931	188	186	2.0
Boiled Linseed Oil (Linoleate Type)	0.941	187	172	2.7
Boiled Linseed Oil (Resinate Type)	0.930	186	176	2.2
Blown Linseed Oil	0.968	189	133	2.8
Lithographic Linseed Oil	0.970	199	102	2.7
Soya Bean Oil	0.924	189	129	2.3
Menhaden Oil	0.932	187	158	3.9
Perilla Oil	0.94	188	180	2.0
Tung Oil (Raw)	0.944	183	166	3.8
Tung Oil (Treated)*	0.898*	128*	104*	6.8*
Corn Oil	0.925	191	118	9.5
Cottonseed Oil	0.921	193	105	3.6
Rosin Oil	0.956	27	41	16.7
Whale Oil	0.924	191	148	....
Neutral Petroleum Oil†	0.916	6	12	....

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* Low constants due to presence of over 40 per cent of volatile matter, largely petroleum spirits.

† This oil contained over 20 per cent of petroleum spirits.

The pigment formula selected for the tests had the following composition:

Basic Carbonate-White Lead	20	per cent.
Sublimed White Lead	30	" "
Zinc Oxide	35	" "
Magnesium Silicate	10	" "
Barytes	5	" "

100 lbs. of pigment base ground to a stiff paste in 16 lbs. of linseed oil.

While this pigment formula was not selected as being superior to certain other formulas, it is of a type that has given very fair service in paint tests throughout the country.

The vehicle formulas in the finished paints are as follows:

	Per cent.
No. 1.	
Raw Linseed Oil	100
No. 2.*	
Soya Bean Oil	100
No. 3.†	
Menhaden Oil	100
No. 4.	
Raw Linseed Oil	25
Boiled Linseed Oil (Resinate)	75
No. 5.	
Raw Linseed Oil	25
Boiled Linseed Oil (Linoleate)	75
No. 6.	
Raw Linseed Oil	50
Boiled Linseed Oil (Resinate)	50
No. 7.	
Raw Linseed Oil	50
Boiled Linseed Oil (Linoleate)	50
No. 8.	
Raw Linseed Oil	50
Blown Linseed Oil	50
No. 9.	
Raw Linseed Oil	50
Litho. Linseed Oil	50
No. 10.	
Raw Linseed Oil	50
Soya Bean Oil	50
No. 11.	
Raw Linseed Oil	50
Menhaden Oil	50
No. 12.	
Raw Linseed Oil	50
Perilla Oil	50
No. 13.	
Raw Linseed Oil	50
Treated Tung Oil	50

---

* Dry pigment formula in soya bean oil.

† Dry pigment formula in menhaden oil.

	Per cent.
No. 14.	
Raw Linseed Oil	50
Corn Oil	50
No. 15.	
Raw Linseed Oil	50
Cottonseed Oil	50
No. 16.	
Raw Linseed Oil	50
Rosin Oil	50
No. 17.	
Raw Linseed Oil	50
Whale Oil	50
No. 18.	
Raw Linseed Oil	75
Soya Bean Oil	25
No. 19.	
Raw Linseed Oil	75
Menhaden Oil	25
No. 20.	
Raw Linseed Oil	75
Perilla Oil	25
No. 21.	
Raw Linseed Oil	75
Treated Tung Oil	25
No. 22.	
Raw Linseed Oil	75
Corn Oil	25
No. 23.	
Raw Linseed Oil	75
Cottonseed Oil	25
No. 24.	
Raw Linseed Oil	75
Rosin Oil	25
No. 25.	
Raw Linseed Oil	50
Soya Bean Oil	25
Menhaden Oil	25

	Per cent.
No. 26.	
Raw Linseed Oil	50
Soya Bean Oil	25
Treated Tung Oil	25
No. 27.	
Blown Linseed Oil	50
Soya Bean Oil	50
No. 28.	
Raw Linseed Oil	25
Soya Bean Oil	25
Menhaden Oil	25
Treated Tung Oil	25
No. 29.	
Raw Linseed Oil	25
Soya Bean Oil	25
Menhaden Oil	25
Corn Oil	25
No. 30.	
Raw Linseed Oil	25
Soya Bean Oil	25
Menhaden Oil	25
Cottonseed Oil	25
No. 31.	
Raw Linseed Oil	25
Soya Bean Oil	25
Menhaden Oil	25
Rosin Oil	25
No. 32.	
Raw Linseed Oil	25
Soya Bean Oil	25
Treated Tung Oil	25
Rosin Oil	25
No. 33.	
Raw Linseed Oil	20
Soya Bean Oil	20
Treated Tung Oil	20
Menhaden Oil	20
Cottonseed Oil	20

No. 34.

	Per cent.
Raw Linseed Oil	20
Soya Bean Oil	20
Treated Tung Oil	20
Menhaden Oil	20
Rosin Oil	20

No. 35.

Raw Linseed Oil	40
Soya Bean Oil	20
Corn Oil	20
Cottonseed Oil	20

No. 36.

Whale Oil	33
Treated Tung Oil	33
Raw Linseed Oil	33

No. 37.

Raw Linseed Oil	25
L. O.*	75

No. 38.

Raw Linseed Oil	50
Raw Tung Oil	50

---

* Mixture of boiled tung and soya bean oil, thinned with petroleum and turpentine.

No. 39.

	Per cent.
Raw Linseed Oil	75
Reducing Oil*	25

No. 40.

Raw Linseed Oil	50
Soya Bean Oil	35
Neutral Petroleum Oil	15

No. 41.

Raw Linseed Oil	50
Soya Bean Oil	25
Neutral Petroleum Oil	15
Tungate Drier	10

No. 42.

Linseed Oil	25
Soya Bean Oil	37
Neutral Petroleum Oil	23
Tungate Drier	15

No. 43.

Raw Linseed Oil	25
Soya Bean Oil	37
Whale Oil	19
Tungate Drier	19

---

* 25 per cent. Raw Linseed Oil.
72 per cent. Petroleum Oil.
3 per cent. Drier — lead and manganese linoleate.

No. 44.

Special test on white base of the following composition, in pure linseed oil:

Asbestine	10 per cent.
Corroded White Lead	20 " "
Sublimed White Lead	30 " "
Zinc Oxide	40 " "

Upper board of panel reduced with straight turpentine on priming coat.

Second board of panel reduced with wood turpentine on priming coat.

Third board of panel reduced with pine oil on priming coat.

Bottom board of panel reduced with petroleum spirits on priming coat.

No. 45.

Same pigment formula as No. 44, reduced with:

Pine Oil	50 per cent.
Linseed Oil	50 “ “

No. 46.

Special test of white base of the following composition, in pure linseed oil:

Corroded White Lead	20 per cent.
Sublimed White Lead	30 “ “
Zinc Oxide	35 “ “
Asbestine	15 “ “

Formulas added to tests during 1913:

No. 47.

Same pigment formula as No. 1.

Vehicle.

Sunflower Oil	50 per cent.
Raw Linseed Oil	50 “ “

No. 48.

Same pigment formula as No. 1.

Vehicle.

Lumbang Oil	50 per cent.
Raw Linseed Oil	50 “ “

No. 49.

Same pigment formula as No. 1.

Vehicle.

Hempseed Oil	50 per cent.
Raw Linseed Oil	50 “ “

No. 50.

Same pigment formula as No. 1.

Vehicle.

Sardine Oil	25 per cent.
Shark Oil	25 “ “
Raw Linseed Oil	50 “ “

Repainting Tests on Paint Oils, with Notes on the Changes Occurring in Oils upon Aging.—Realizing that the results of repainting tests are much more conclusive than the results from

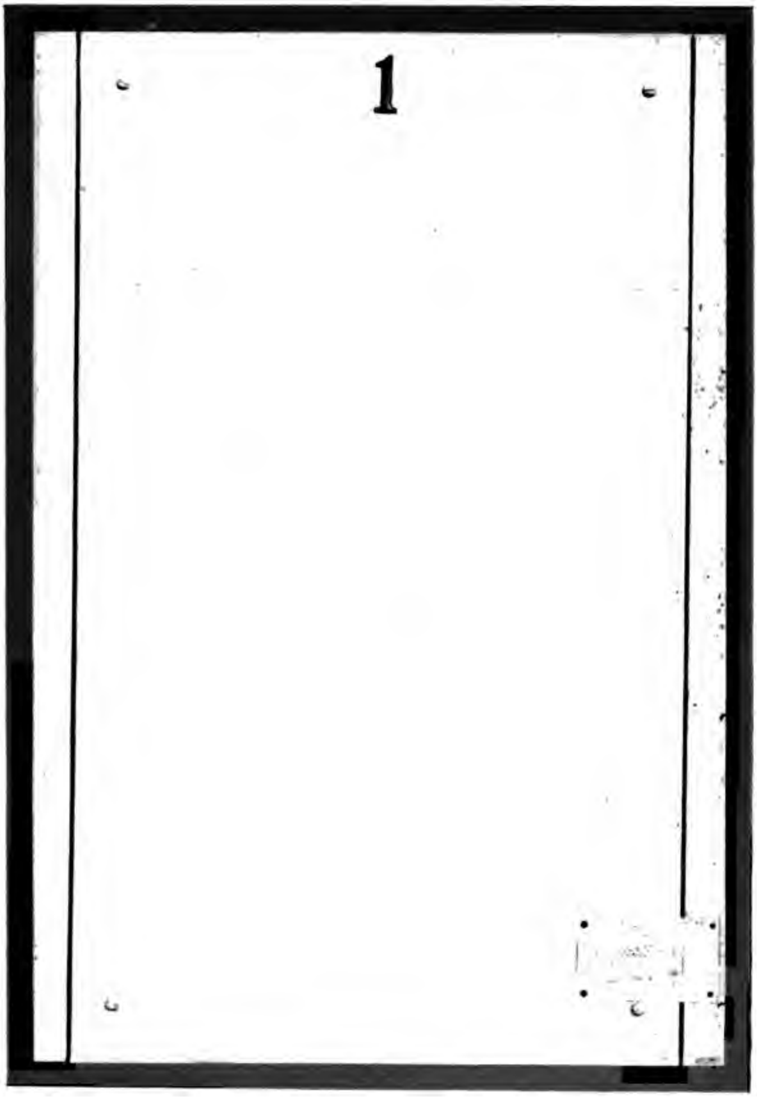

FIG. 29.

Appearance of One of the Repainted Panels.

primary paintings, the tests on paint oils were repainted in October and November, 1914, after having weathered for three and a half years. At definite periods, previous to repainting, careful inspections had been made of these tests and photographic records of the appearance of each paint were made.

Method of Repainting.—Previous to repainting, the surface of each panel was lightly sanded with No. 00 paper to remove any surface defects or accumulated stains. The paint was then applied directly to the panels upon the exposure rack, by a competent painter. To cause more rapid drying, and thus minimize the danger of adherence of insects and atmospheric dust, five per cent of drier was added to each paint. For the first coat, reduction with a pint of turpentine to a gallon of paint was made. The second or finishing coat was applied without reduction. The amount of paint required for each coat was accurately determined, but no definite spreading rate was adopted, each panel being allowed sufficient paint to thoroughly satisfy the surface. A period of one month was allowed for drying between coats. The first coat was applied on October 2 and the final coat on November 5, 1914.

Preparation of Paints.—As none of the paints used for the original painting of the panels had been reserved, it was necessary to make up another quantity of each for the repainting tests. For this purpose a quantity of the original white pigment mixture, ground to a stiff paste in fourteen parts of raw linseed oil, was prepared. Weighed amounts of this paste were thoroughly mixed with the various oils required to make up the formulas, as shown above. The paints were contained in friction-top cans. Samples have been reserved for future reference and observation.

Physical Properties of Oils.—In preparing the paints for the repainting tests, it became apparent to the writer that some oils possess greater lubrication qualities than others. For instance, it was found that some of the semi-drying oils formed very easy working paints, and that lesser amounts of such oils than of some others produced paints of a desired body.

The working of these paints under the brush was good, but some had a slippery feeling and their application resulted in rather thin coats. All of the paints to which heavy-bodied or heat-treated oils were added, worked rather hard and produced comparatively thick films of a glossy character. In the repainting tests Formulas 8, 9 and 27 required the addition of 8 per cent of turpentine to assist spreading. The writer also observed that the color of the oil used has considerable to do with the appearance of a finished paint. For instance, some oils exhibit a clear, green color (*probably due to the presence of dissolved chlorophyll, the coloring matter which is responsible for the color of vegetation*). Such oils, when mixed with a white pigment, produced paints of greater apparent whiteness than when yellow or dark amber-colored oils were used. The green color in the oil apparently acts in a like manner to ultramarine blue, a pigment which is sometimes added in small percentage to some off-color white substances to simulate the appearance of a clear white.

Chemical Changes in Oils.—Many of the oils used in preparing the different formulas were portions of the quantities originally used in the first set of paints. Analysis of these oils showed that some action had occurred in them during the interval, their constants in some cases varying from the constants shown when the oils were first analyzed. (See Tables 2 and 3.) It was necessary in a few instances, where the supply of the original sample was insufficient, to secure fresh quantities of the same type of oils used for the original painting. The change shown in some of the original oils may have been due to partial hydrolysis. Such action generally causes a rise in acidity, gravity, and saponification value and a drop in the iodine value. Partial oxidation might also account for some of the changes shown, although the oils were kept in stoppered containers. In some cases the amount of oil in a container occupied less than one-half the interior space. The air contained above the oil might in such instances have some effect in causing changes in the oil below. In one instance, that of the Special Perilla Oil, a most marked change had taken place. The original sample of oil was obtained from China

When the can was opened at the time of original painting the oil was limpid and of the appearance of ordinary raw linseed oil. At that time, over half of the oil was removed for examination and the can loosely stoppered. When examined in the fall of 1914, the oil was of the consistency of soft jelly and flowed with difficulty. The color was very much lighter than when first examined. A remarkable change had taken place in the oil, as the analysis shows. This change, in the writer's opinion, was due either to autopolymerization or to bacterial action. In an investigation* the writer pointed out the effect of enzymes upon oils and oil paste paints, and showed that such effects may be inhibited by sterilization. Perilla oil has a very high iodine number and is an excellent drying oil. If it should be produced in sufficient quantity, either in China or America, it will probably prove very useful in varnish as well as paint manufacture. The writer has already made small kettle tests which show that perilla oil is capable of bodying up under heat and uniting with resins to form good varnishes.

Additional Tests.—There were added to the tests during the early part of 1913 four panels (47-50) painted with additional oils secured at that time. These panels were also included in the repainting test.

After repainting, the panels were all striped, numbered, and labeled with cards bearing the formulas of the paints applied, and other data which might be useful to inspectors.

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* Changes Occurring in Oils and Paste Paints Due to Autohydrolysis of the Glycerides, p. 286.

TABLE 6.

Comparative Analyses of Oils Used for Tests.

Analyses were made when oils were first obtained and 42 months later, at the time they were used in repainting tests. Chemical changes occurring in the oils are recorded by the constants.

	Sp. Gr.	Iodine No.	Sapon. No.	Acid No.	Refrac. Index.
Raw Linseed Oil—					
March, 1911	.931	186	188	2.0	
November, 1914	.933	185.4	189.6	2.8	1.4867
Soya Bean Oil—					
March, 1911	.924	129	189	2.3	
November, 1914	.925	130.2	193.1	4.7	1.4813
Menhaden Oil—					
March, 1911	.932	158	187	3.9	
November, 1914	.934	156.3	193.7	16.1	1.4850
Raw Tung Oil—					
March, 1911	.944	166	183	3.8	
November, 1914	.946	161.5	190.3	5.7	1.5050
Perilla—					
March, 1911	.94	180	188	2	
November, 1914	.94	172	195.4	7.4	1.4874
Perilla Special*—					
March, 1911	.94	192	189	3.2	
November, 1914	.981	123.8	219.4	20.8	1.4978
Heavy Bodied Linseed Oil—					
March, 1911	.968	153	189	2.8	
November, 1914	.992	130.5	200	6.3	1.4966
Lithographic Linseed Oil—					
March, 1911	.97	102	199	2.7	
November, 1914	.96	103.4	150.9†	13.4	1.4978
Whale Oil—					
March, 1911	.924	148	191	9.2	
November, 1914	.926	138.2	191.2	17.4	1.4820
Boiled Linseed Oil (Linoleate Drier)					
March, 1911	.941	172	187	2.7	
November, 1914	.943	170	188	3.1	1.4895

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* Referred to in text.

† Low saponification number due to formation of small amount of linoxin or other difficultly saponifiable substance.

TABLE 7.

Analyses of Additional Oils Obtained for Repainting Tests.

Analyses made November, 1914.

	Sp. Gr.	Iodine No.	Sapon. No.	Acid No.	Refrac. Index.
Corn Oil	.921	124.8	190.1	4.1	1.4800
Cottonseed Oil	.920	111.7	194.3	0.9	1.4781
Rosin Oil	.964	68.9	35.5	32.4	....
Treated Tung Oil*	.882	56.4	101.3	7.7	1.4764
Lumbang Oil	.927	152	189	1.0	1.4789
Sunflower Oil	.924	124.6	189.3	7.5	1.4796
Hempseed Oil	.927	149.4	191.1	3.9	1.4822
Shark Oil	.910	132.8	158.9	5.2	1.4815
Sardine Oil	.919	134.6	177.3	10.4	1.4800
Petroleum Mixing Oil	.851	28.2	52.9	1.1	1.4773
Boiled Linseed Oil— (Resinate Drier)	.936	184.2	187.6	7.3	1.4895

* Contains 30% volatile matter, largely high boiling point petroleum spirits.

Results of Tests.—A summarized report of the condition of each panel at every annual inspection for five years is now in print.* A page of this report is appended. In conclusion, it may be stated that linseed and perilla oils gave most satisfactory results. Certain mixtures of these oils with soya, lumbang, corn, cottonseed and sunflower oils also gave very good results. Boiled oils containing driers proved less durable than the same oils in the raw state. Blown and bodied oils have added to the gloss of paints and have not detracted materially from their durability when an excess of thinner has not been used. Marine animal oils, when used in quantity, have caused marked retention of dust and softening of film in damp weather. Treated tung oil has caused cracking. Fixed petroleum oils have proved unsatisfactory. Rosin oil has caused disastrous effects when used in any percentage.

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* Bull. 53, Scien. Sec., Paint Mfrs.' Ass'n of U. S.

TABLE 8.

Panel.	Formula.	Year.	Color.	Chalking.	Checking.	General Film Condition.	Remarks.
1	100% Raw Linseed Oil	1912	White	Very slight	None	Excellent	White and clean.
		1913	Very white	Medium	Slight	Good	Very white, clean surface. Few slight cracks on upper board.
		1914	White	Medium	Some	Fairly good	Slight scaling shown on top and lower boards.
		R-1916*	White	Medium	None	Excellent	
		R-1917	White	Medium	None	Excellent	Cracking and scaling on upper board only.
2	100% Soya Bean Oil	1912	Darkened	Very slight	Slight	Very good	Film not as hard as No. 1 paint.
		1913	Very dark	Medium	Medium	Good	Although panel is in good condition, with the film practically intact, paint has become dark on account of the semi-drying nature of the oil, which holds particles of soot deposited on surface.
		1914	Fairly white	Considerable	Medium	Fairly good	Slight cracking on lower and upper boards.
		R-1916	Slight darkening	Medium	Medium	Fairly good	
		R-1917	Fairly white	Slight	Medium	Fairly good	

*R — abbreviation for "Repainting Tests."

CHAPTER VI.

PAINT PROTECTION FOR PORTLAND-CEMENT SURFACES.

Another interesting series of exposure tests of paint made at The Institute of Industrial Research in Washington were designed to throw light on the subject of painting cement.

In many instances it has been found desirable to decorate certain kinds of Portland-cement structures with moisture-proof coatings.* The appearance is thereby made more pleasing and the cement is protected from the destructive action of the elements.

The author has occasionally come across statements which would tend to create an impression to the effect that Portland-cement surfaces are highly alkaline and cannot be satisfactorily decorated with oil paints. That such an impression is incorrect, seems to be the opinion of all investigators who have made painting tests of an extended nature. In fact, there is much evidence to show that Portland-cement surfaces are quite as well suited to receive paint coatings as iron, wood and other kinds of structural materials. Moreover, the results of well-conducted tests have shown that pure oil paints, such as are used upon wooden structures, may be used with equal satisfaction upon cement.

That the painting of cement is not a new art is evident from the many references in the literature which describe methods of decorating and rendering damp-proof all classes of cement. Soon after Portland cement came into general use, it was customary to decorate certain kinds of constructions made from this material, the prevailing method being to apply varnishes containing copal, shellac, rosin or other resins, admixed with oil, turpentine and benzine. Subsequent to the application of such primers, a finishing coat of enamel made by grinding color pigments with the primer, was then applied. The principles underlying these old methods have since been followed with varying success, and up until a few years ago it was a common procedure for painters to apply a coat of varnish suction primer to cement and plaster walls previous to painting them. Surfaces thus treated were filled, made less absorptive and from this standpoint in a somewhat better condition than bare walls to receive the final coat of paint or enamel.

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* This does not refer to treating cement masonry which is subjected to hydrostatic pressure and which may be in a very wet condition. Such masonry requires waterproofing rather than moisture-proofing treatment.

The suction varnishes or fillers made for this purpose were of two classes. One widely used was made of rosin dissolved in benzine and admixed with linseed oil. The rosin was sometimes made more suitable by dissolving therein certain drying agents such as red lead or lime. Lead or calcium resinate would thus be contained in these fillers. Varnishes made of the more expensive resins, such as Manila and copal, have also been used for the same purpose.

Whether these suction varnishes actually enter into chemical combination with the lime or other materials in cement or plaster, or whether they simply act as insulation coats, is a matter which has received considerable attention. If chemical reaction really occurs when a varnish coating is applied to cement, varnishes of the highest acidity, such as those made of colophony resin (common rosin), would be most efficient as lime neutralizers and better suited as primers, provided the durability of the coating is dependent upon the amount of calcium resinate which might be formed. Varnishes which have been prepared from the expensive resins generally show an acid number of from 5 to 10, while varnishes made from colophony resin (rosin) generally have an acidity of from 40 to 80. The author is inclined to doubt the possibility of lime neutralization by the use of suction varnishes. It is not a simple matter to produce calcium resinate under the most favorable conditions. Even molten rosin of 150 acidity requires prolonged heating at a high temperature, in order to take up as little as 2 to 3 per cent of lime. When a varnish of low or high acid value is applied in the cold to a cement surface, drying occurs in an exceptionally short time, and there is no opportunity for the small proportion of resin present in such an extremely thin coating, to effect a reaction which even at high temperatures takes place with the greatest difficulty. The effect which is really produced when a varnish is applied to a cement surface is not chemical, but of a physical nature, the varnish having a binding and filling effect upon the cement, similar to the binding and filling effect which is produced by the application of certain types of oils to cement surfaces.

Probably too much importance has been attached to the alleged destructive action of lime in cement surfaces. It is well known that setting Portland cement develops free lime, but the amount to be found upon a Portland-cement structure should be considered as negligible in most instances, as far as it might affect a well-designed paint. If indeed it is advisable to neutralize this small amount of lime, previous to painting the cement surface, such a result is not to be properly accomplished with an organic substance but rather with an inorganic material which readily reacts therewith. A solution of zinc sulphate* (Macnichol's method) has proved most efficient for this purpose and has been used for many years with practical results, especially upon freshly laid cement. It might be well to point out at this place that the priming or ground-coating of cement is often improperly carried out, when clear primers of any kind are used. If, for instance, a clear varnish is applied to a cement surface, the primed surface is difficult to differentiate from the untreated area. Consequently, the workmen using clear primers often leave untreated laps or "holidays," as they are technically known. For this reason, the use of color primers should be adopted wherever possible.

The dusting of cement floors, which is brought about by abrasion, may be effectively stopped through the use of oil-pigment paints. If the floor has been freshly laid and is damp, the possibility of lime reaction may be removed by treating the surface with a solution of tinted zinc sulphate. The oil paint may then be applied. Boiled linseed oil, sometimes mixed with tung oil, may be used as the liquid portion of the paint. These oils have a remarkable binding action when applied to a cement surface. When mixed with pigment, they form paints which are eminently suited as first coaters for cement floors. The first coat will dry rapidly and form a dense surface. Over this may be applied a second coat and, if a high gloss surface is desired, a portion of varnish may be added to this final coat. The various floors of the author's laboratory were treated in this fashion, with prepared floor paints made from such materials, one week after the placement of the cement. The zinc-sulphate primer was used only upon the damp areas. The floors have since been subjected to much abrasion from constant walking and the moving of heavy apparatus. Oils and chemicals of various kinds have come in contact with the floors, and soap and water have been used upon them very often for cleaning purposes. After five years' continued service, the floors have not dusted and have just been repainted. This service record would tend to show that placed Portland cement may be made dust- and wear-proof and highly desirable as a flooring material, through the application of oil paints.

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* Proceedings, Am. Soc. Test. Mats., vol. X, pp. 395-400 (1910).

In April, 1912, the writer instituted a series of tests to determine the durability of various types of paint upon Portland-cement surfaces exposed to the weather. The panels for the tests were prepared by constructing a long board wall to which was fastened expanded metal. A mixture of 1 part of Portland cement and 2 parts of clean Potomac River sand was made and applied to the expanded metal, forming a cement wall 3 in. in depth. The wall was divided into 35 sections or panels, each 30 in. wide and 40 in. high. Three coats of paint were applied to each panel by a practical journeyman painter. In order to make the test more severe, nearly all of the paints were applied in white. (Tinted paints are known to be much more durable than white paints.) A stripe of chrome green, 6 in. wide, was placed over the top of the third coat of paint, in order to determine whether the lime which might be present on the surface of the cement would have any effect upon the paint coating. Fading of the green to a yellow would indicate such action.

The general results of the tests at the end of a 2-year period, together with an outline of the composition of the paints tested, are given as follows:

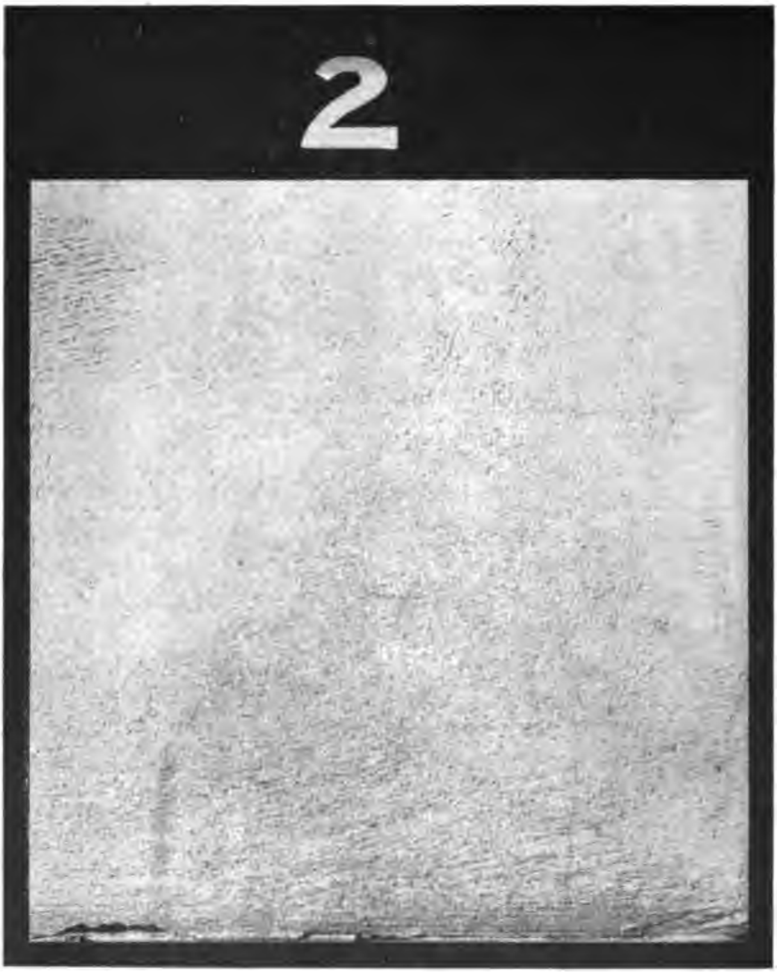

FIG. 30.
PANEL 2—Single Pigment Paint made with pure linseed oil. Condition good, but surface has darkened.

Class No. 1.—Single-pigment paints made with white lead or zinc oxide ground in pure linseed oil.

These paints are in very good condition throughout (see Figs. 30 and 31). The sublimed white lead paint is superior to the others. It presents a very white surface and is giving excellent protection to the cement (see Fig. 31, Panel No. 3).

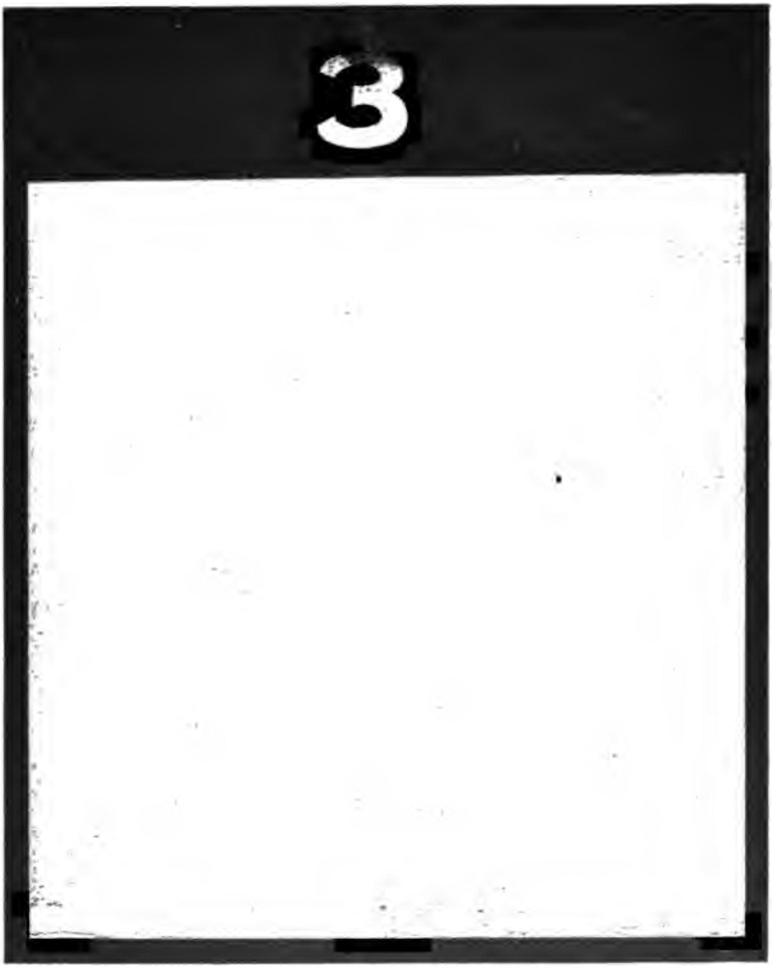

FIG. 31.
PANEL 3—Single Pigment Paint made with pure linseed oil. Condition good.

Class No. 2.—Combination-pigment paints made of mixtures of white lead, zinc oxide or similar pigments ground in pure linseed oil.

These paints are in generally excellent condition (see Figs. 32 and 33).

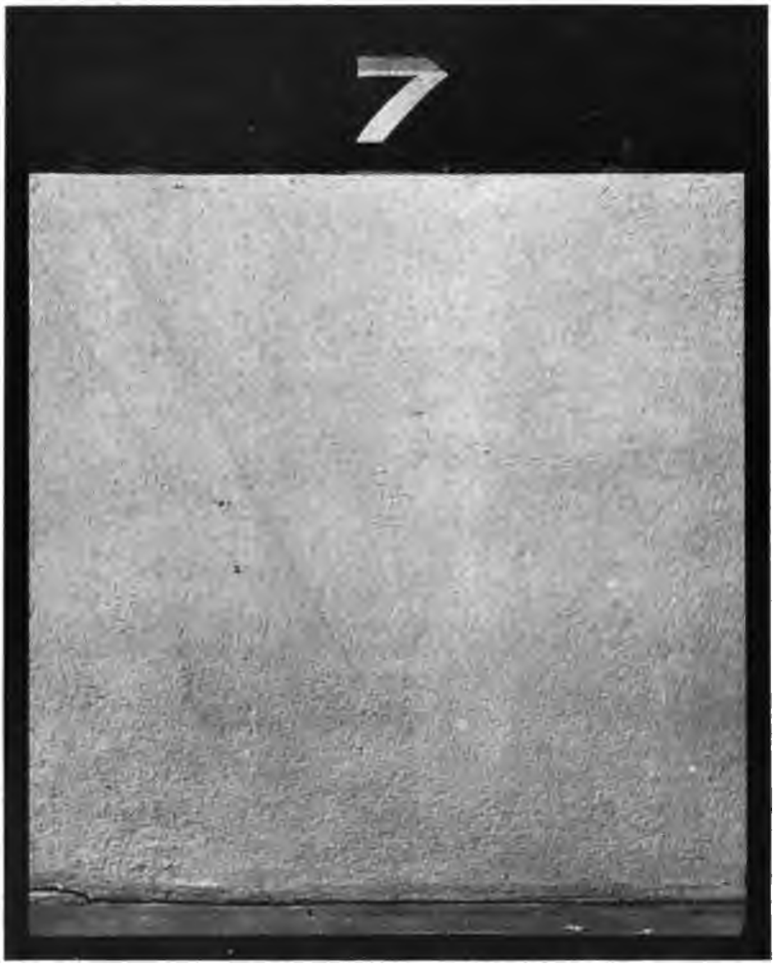

FIG. 32.
PANEL 7—Combination Pigment Paint made with pure linseed oil. Excellent condition.

Class No. 3.—Combination-pigment paints ground with mixtures of raw and heavy-bodied linseed oil or with treated tung oil. The viscosity of these oils requires the use of considerable turpentine or other thinner in the manufacture of such paints, in order to make them of the right viscosity for

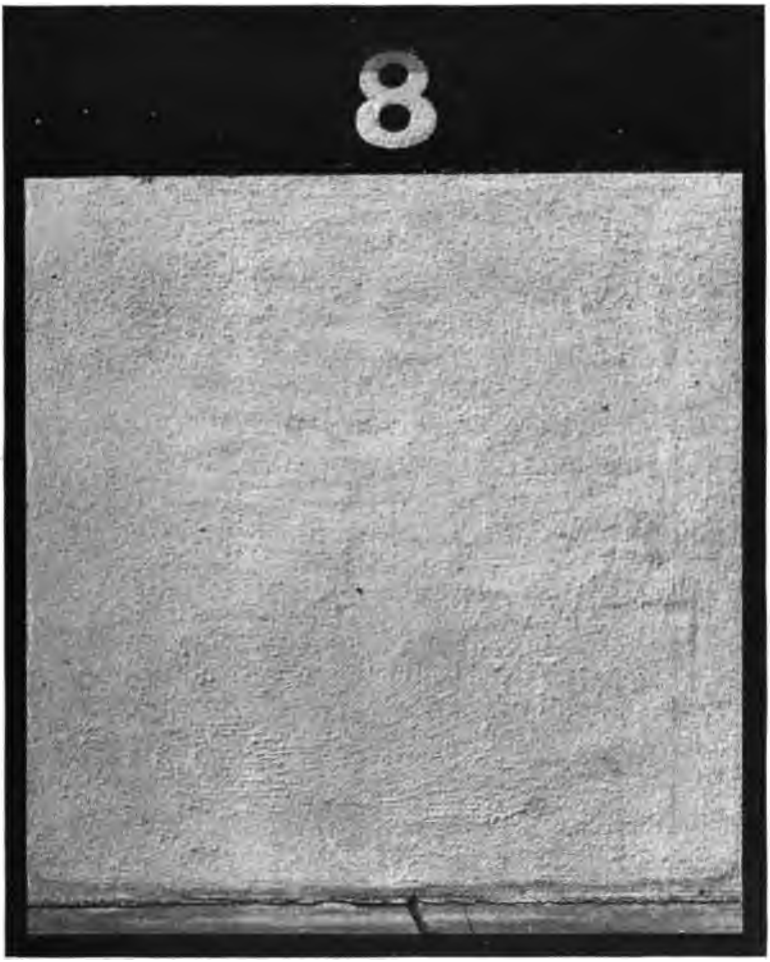

Fig. 33.

Panel 8—Combination Pigment Paint made with pure linseed oil. Excellent condition.

application. Semi-flat surfaces are therefore produced during the drying. Such a finish is often preferred to a gloss surface.

Most of these paints are in excellent condition (see Figs. 34 and 35).

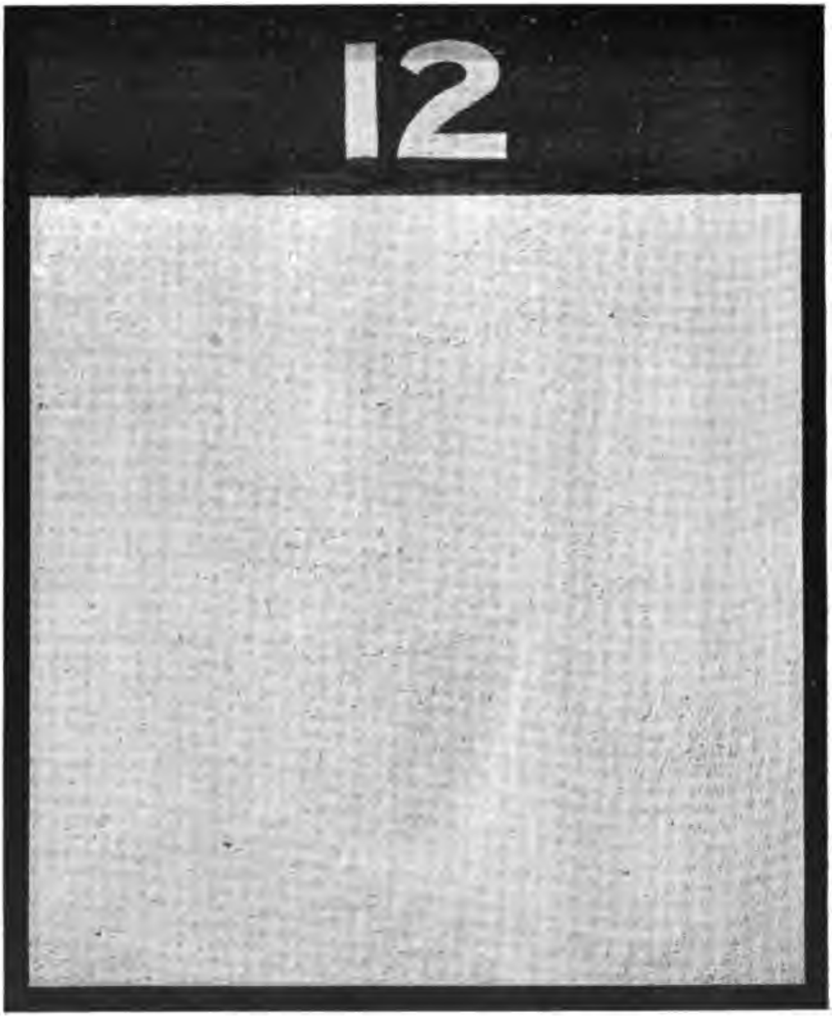

FIG. 34.

PANEL 12—Combination Pigment Paint made with mixture of Raw and Bodied Oils. Excellent condition.

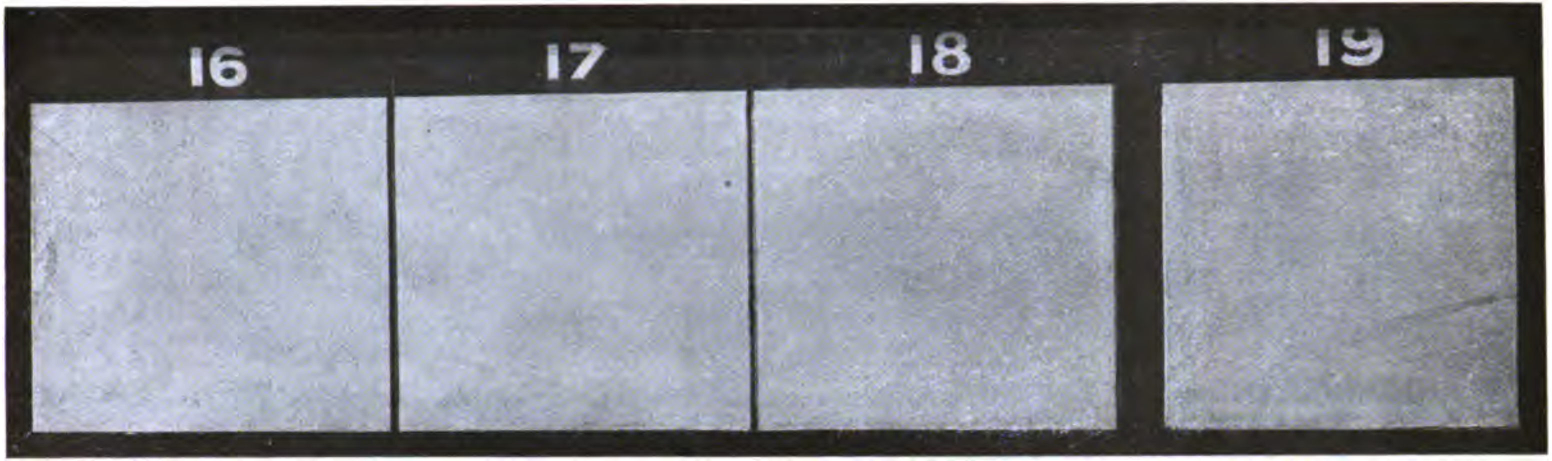

FIG. 35.

PANELS 16 TO 19—Combination Pigment Paints made with heated and treated linseed and tung oil. Excellent condition.

Class No. 4.—Single and combination pigments ground in oil varnishes containing acid resins.

These paints are checking and scaling in many spots. Such varnish paints are apparently not suited to exterior exposure (see Figs. 36 and 37).

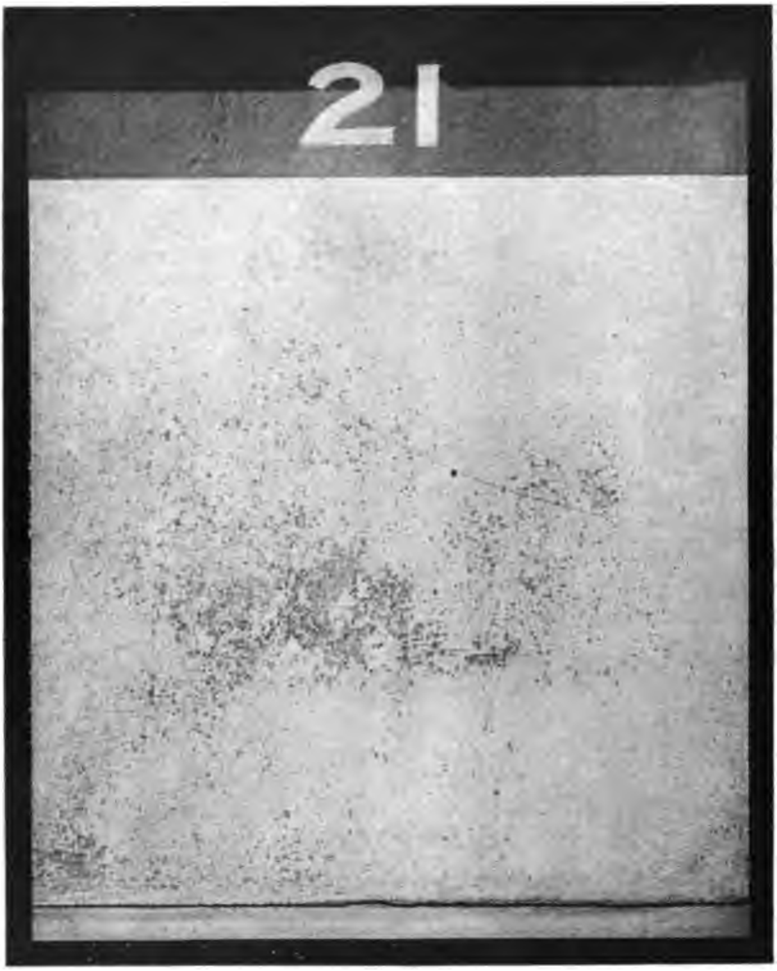

FIG. 36.

PANEL 21—Varnish Paint containing Acid Resin. Scaling and surface disintegration shown.

Class No. 5.—Paints containing resins dissolved in volatile spirits (spirit varnishes) with or without pigments.

These paints are not giving very satisfactory service, the clear varnishes having entirely decayed in some cases. Those to which pigment has been added are in somewhat better condition.

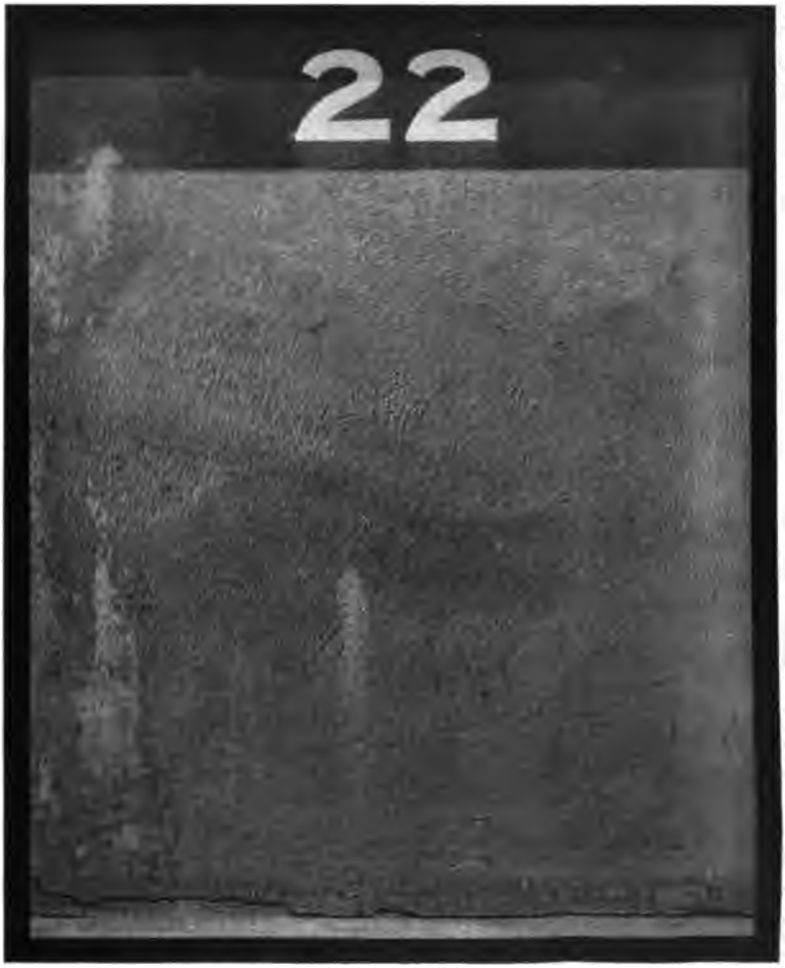

FIG. 37.

PANEL 22—Varnish Paint containing Acid Resin. Scaling and surface disintegration shown.

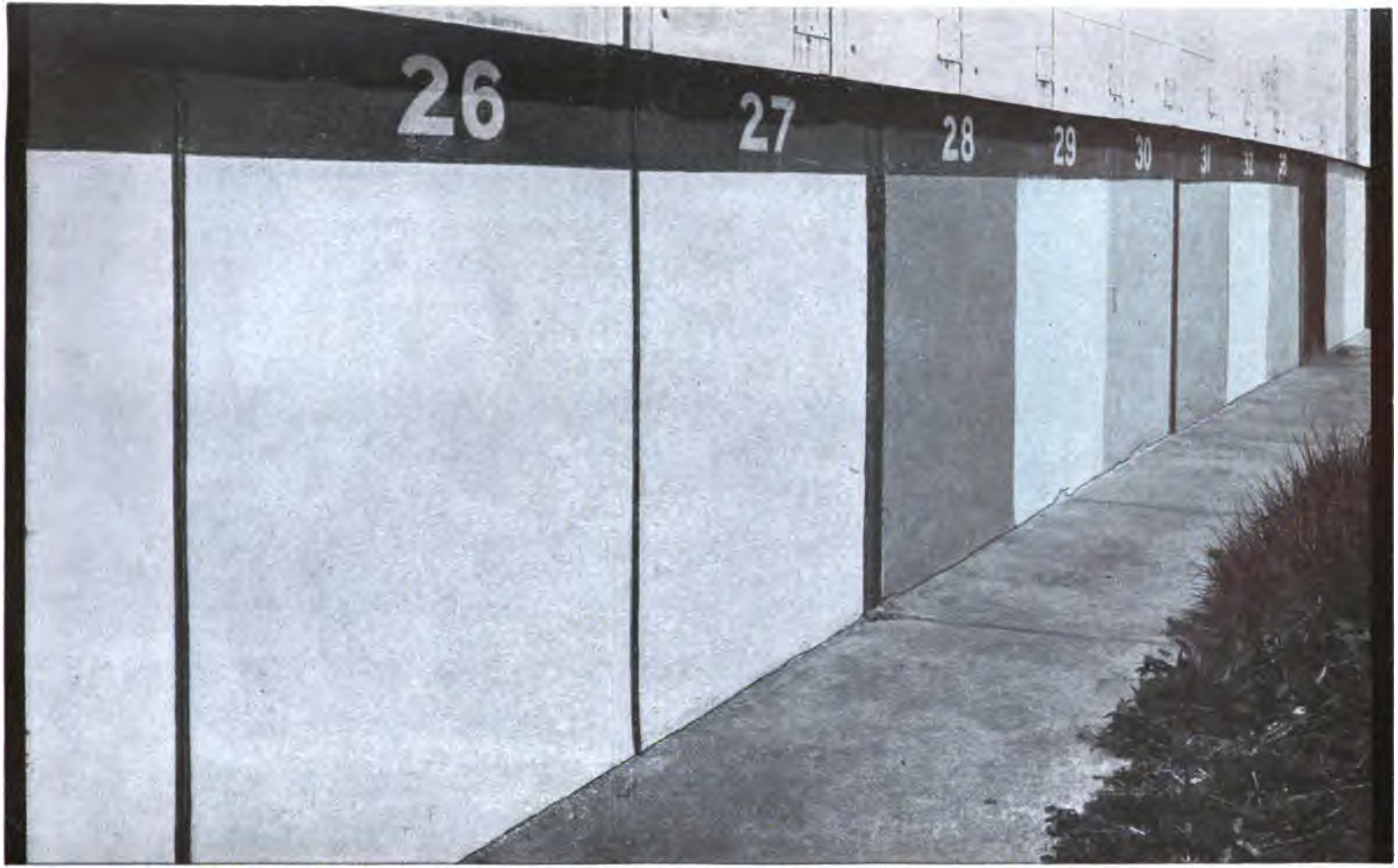

FIG. 38.

View of various Prepared Paints on Cement Surfaces. Most of these paints are made of Combination Pigments ground in mixtures of raw and heavy-bodied linseed oil or treated tung oil. This type is in excellent condition.

Class No. 6.—Paints made with single and combination pigments ground in a water medium containing glue or casein as a binder.

These paints are chalking rapidly and are not moisture-proofing the cement. The pigment binder has been destroyed by the weather.

Opaque white pigments, such as basic sulphate-white lead, basic carbonate-white lead, zinc oxide, and lithopone, were present in the paints which gave the best results. In some of these paints there was also present a percentage of inert pigments, such as barytes, asbestine, whiting, china clay, gypsum and silica.

The results of these tests are quite in line with the results obtained by Ware and Schott* in a series of paint exposure tests made upon exterior concrete surfaces. They also agree with previous long-time exposure tests made by the author.

As a result, therefore, it can be stated that concrete surfaces may be decorated with excellent results through the use of high-grade oil paints. When the cement surface is freshly laid and damp, such paints may be safely applied after treating the cement with a zinc-sulphate primer.

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* "Paint Films as Protective Coatings for Concrete." *Journal of Industrial and Engineering Chemistry*, vol. VI, No. 3, p. 184 (March, 1914).

CHAPTER VII.

PAINTS TO PREVENT ELECTROLYSIS IN CONCRETE STRUCTURES.

The use of protective paints upon metal that is to be embedded in concrete structures, in order to prevent any damage which might be caused by electrolysis, has been proposed from time to time. No tests had been made, however, as far as the writer is aware, to determine what type of coating is best suited for the purpose previous to those described below. It would appear from first consideration that a paint capable of forming a film of high electrical resistance would be most efficient. Such films, however, generally present a high gloss surface and are apt to prevent the proper bonding of the concrete with the painted metal, thus doing more harm than good. It is chiefly for this reason that engineers have not generally adopted the use of paint upon reinforcing metal. In the experiments presented herein, a method for overcoming this objectionable feature of insulating paints is described, and data are presented on the relative insulating and bonding values of several different types of paint.

Corrosion Causes.—Before describing these tests, it might be well to review briefly, for the benefit of those not thoroughly familiar with the subject, some of the conditions upon which metal corrosion depends. The ordinary forms of iron corrosion have been found to be due to auto-electrolysis, the presence of segregated impurities being responsible for differences in potential at certain areas, which set up galvanic action and cause solution and the formation of rust at the positive nodes. A similar but more rapid action takes place when an electric current is passed through an iron anode immersed in an electrolyte; *e. g.*, salt water. When damp cement contains an embedded iron anode, the cement acts as an electrolyte and the same rusting action takes place, regardless of the fact that concrete contains sufficient lime to inhibit corrosion when no electrical currents are present. With the electrolytic change of metal into oxide comes an increase in volume of the products of reaction, and there is developed an enormous expansive force or mechanical pressure, which is sufficient to crack the strongest forms of concrete.

Source of Currents.—Corrosion may therefore be expected, with its attendant results, when sufficiently high-voltage direct currents enter the iron of a new concrete building, either through contact with conductors of light and power circuits, contact with water or gas pipes carrying direct currents from grounded power lines, through defective insulation of electrical wiring, or from similar sources. That the damage is greatest to new structures is due to the fact that the concrete is then damp and a better electrolyte than when it has become dry from age. That examples of reinforced concrete structures damaged from stray currents are not more common may be due to the fact that in many localities engineers are active in their endeavors to prevent high-voltage currents from running wild. This fact, however, does not justify a disregard of what might happen in the future and what may now be happening to some structures which have not been carefully guarded against stray-current electrolysis. That much of this damage may be prevented by the adoption of suitable forms of foundation water-

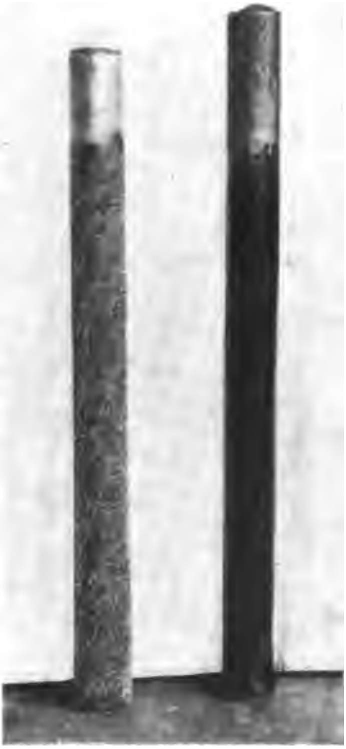

Fig. 39.
Painted Rods.
Specimen at left was "sanded."

proofing, erterior insulating joints for pipe-lines, isolation of lead-covered cables entering buildings, and other insulating devices is shown by Rosa, McCollum, and Peters* in what is probably the most valuable contribution to the subject of reinforcement electrolysis that has ever been published. Of equal importance, however, should be the safeguarding of the metal with suitable insulating and bonding paints, before it is embedded in cement. The adoption of this precaution, if followed by the use of the safety devices noted above, will guard against the causes which contribute to electrolysis and thus render our modern concrete structures safe from destruction by reinforcement corrosion.

Experimental.

Series I.—The writer's investigations were made upon two separate series of concrete test cylinders. The first series were made by embedding, in concrete cylinders, painted iron rods ½ in. in diameter and 12 in. long. Previous to painting, the rods were thoroughly cleaned from scale and rust. Two coats of paint were then applied, allowing a week's time for drying between coats. The painted rods were then placed in molds in an upright position, about 1 in. apart and 1 in. from the bottom of the molds.

Cement mortar, prepared from one part of Portland cement and two parts of sand, was poured around the rods and tamped into place. After two days' time the molds were removed and the test pieces were repaired with cement mortar wherever defects were shown.

Method of Making Good Bonding Surfaces.—In making up the specimens for test, it occurred to the writer that the objection to using paints which dry upon metal to a gloss surface, and which prevent proper bonding of the cement, might be overcome by applying to the painted surface, while it is still tacky (not dry), sharp particles of sand or similar material. Emery powder, abrasives, and fine quartz sand were among the substances tested. When allowed to drain upon a painted rod, the particles become attached to the paint and dry with it to form a rough surface resembling coarse sandpaper (see Fig. 39). After thoroughly drying, the particles are solidly embedded in the paint, which thus presents a dull rather than a gloss film. Fine, clean, white sand was found most useful.

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*"Electrolysis in Concrete," Technologic Paper No. 18, U. S. Bureau of Standards.

Arrangement of Tests.—After aging for a month, the pieces were connected in parallel and in series with resistance to reduce the voltage from 110 to 30 volts D. C. Current readings were made over a period of twenty-four hours. The current passing was small. The test cylinders were then placed in a shallow pan containing sufficient water to immerse the lower 2 in. of each specimen. After a week's test, the cylinders were disconnected and removed from the pan for observation.

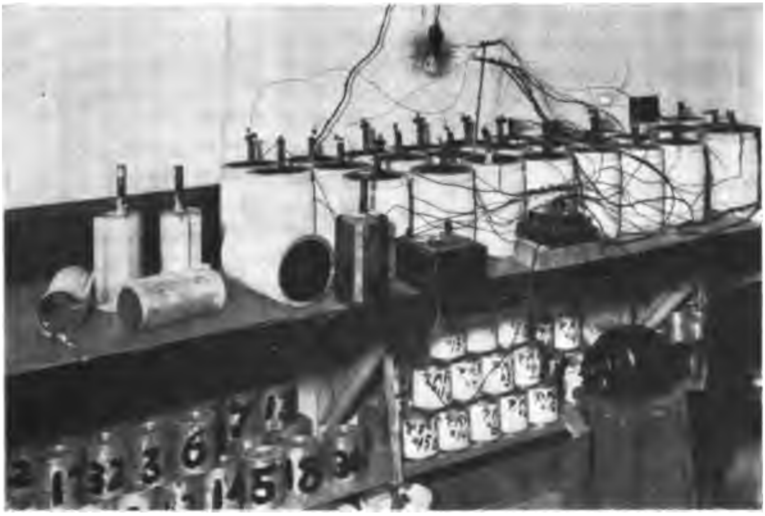

FIG. 40.

ARRANGEMENT OF SERIES II SPECIMENS IMMERSED.

Iron Molds for Forming Specimens Shown at Left.
Specimen Removed From Jar Shows
Surrounding Iron Cathode.

A few of the specimens showed small cracks near the bottom, where the wet cement had conducted the current to the greatest extent. The cylinders were then placed in separate earthenware jars and again connected up. The jars contained sufficient water to immerse the specimens up to within 1 inch of their top surfaces. They were left in circuit for ten days and current readings were made every twenty-four hours. Cracking was shown by nearly every cylinder which current readings proved to be carrying any appreciable amount of current. The fracture in every case started at the anode, extending radially to the edge of the cylinders and parallel to the

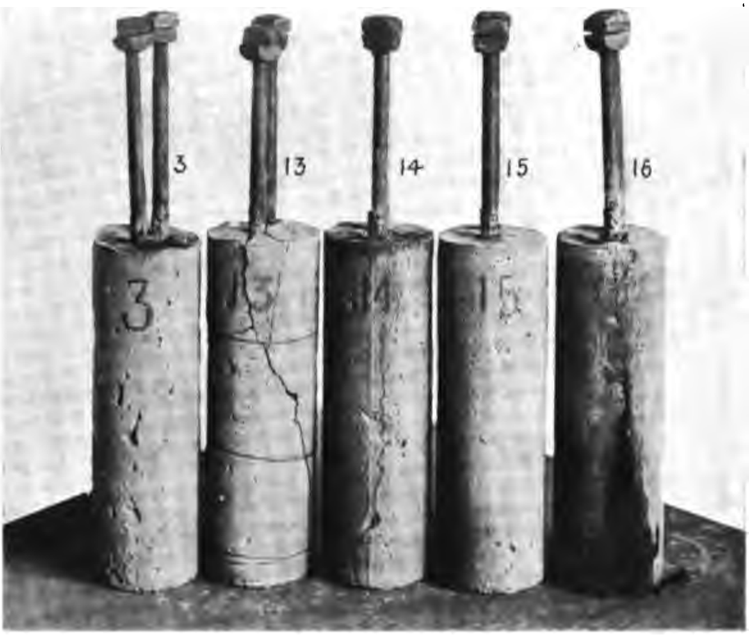

FIG. 41.

PART OF TEST CYLINDERS—SERIES I.

Nos. 3, 13, 14, 15, and 16 contain rods coated with oil-pigment paints. While excellent protection for exposed structural steel, these paints are not so efficient for embedded steel subjected to electrolysis.

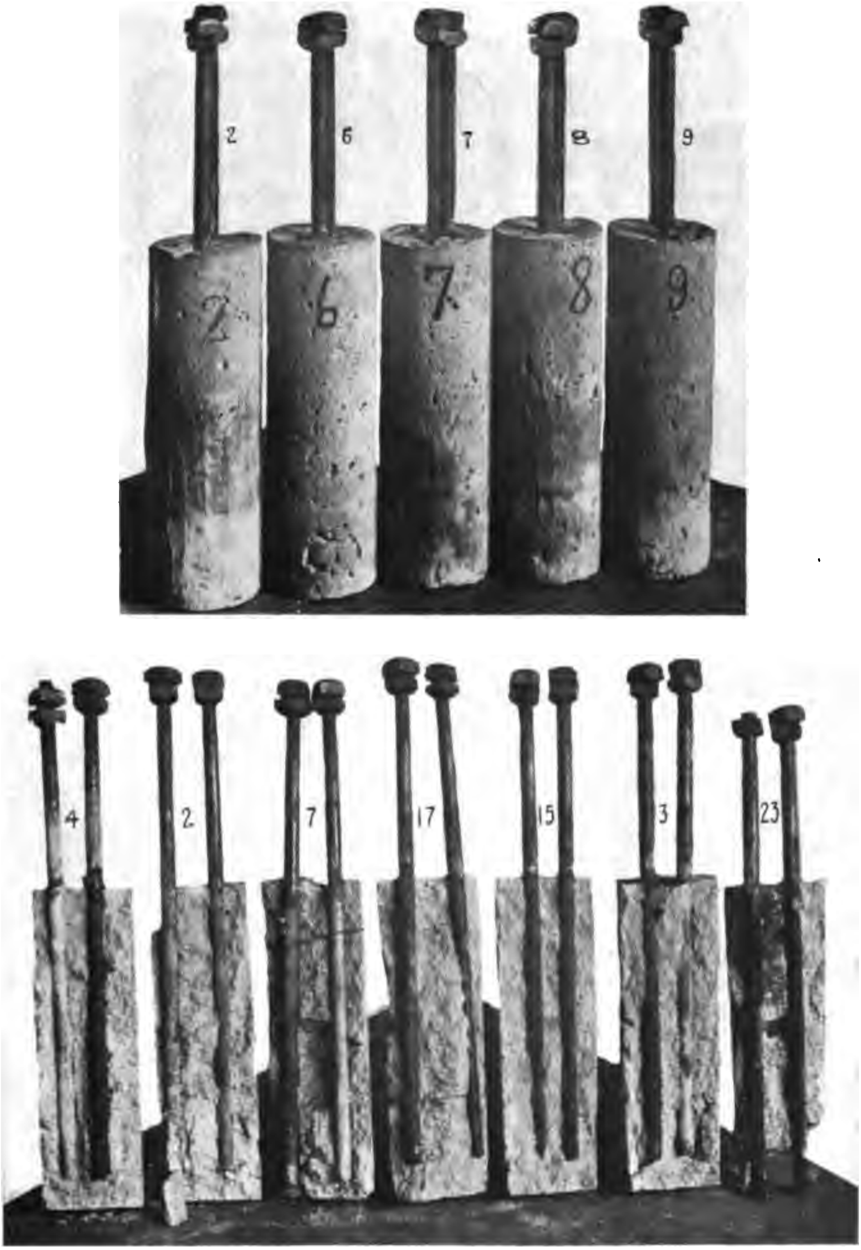

Fig. 42.

Part of Test Cylinders—Series I.

Nos. 2, 6, 7, 8, and 9 contain metal coated with resin or special oil compounds; no cracking occurred; 23 (unpainted) and 4 (water paint) show great corrosion at anode; 3 and 15 (oil paints) show less corrosion; 2 (heat-treated tung oil compound), 7 (sandarac in alcohol), 17 (special bitumen), and 15 (chromated iron oxide in oil) show practically no corrosion.

electrode, gradually opening up as the tests were continued. The specimens were finally disconnected and removed for examination. Those which had been cracked by the electrolytic corrosion of the metal were easily split into two sections, disclosing the contained electrodes. The others, which did not show any cracking, were parted with a chisel, in order to make a comparative examination of the condition of the embedded metal.

Series II consisted of specimens made by embedding in concrete cylinders painted anodes ¾ inch in diameter and 12 inches in length. Previous to painting, the rods were thoroughly cleaned from scale and rust. They were painted with two coats of the same paints used in Series I. The rods were placed in molds 3½ x 8 in., in an upright position, and the same kind of Portland cement mixture used in Series I tests was placed around the rods and tamped into place. The specimens for this series were very carefully prepared and presented a much better appearance than those used in Series II. After setting for two days, the molds were removed from the pieces, which were then aged for a month. They were then placed in water for twenty-four hours, and the next day were put into individual earthenware jars containing sheet-iron cathodes coiled so as to surround but not touch the cylinders. The jars were filled with sufficient water to cover the cylinders up to within one inch of their top surfaces. The specimens were connected up as in Series I. The tests were continued for 240 hours at 30 volts, during which time Nos. 4, 10, 11, 13, 15, 19, and 24 had developed cracks. The voltage was then increased to 55 and continued for 60 hours, at which time the tests were discontinued.

Series III: Test of Bonding Value.—In order to determine the comparative bonding strength shown by the various painted rods with the surrounding concrete, a series of test specimens was prepared, exactly duplicating those used for Series II, except that the rods were placed flush with the bottom surface of each cylinder. After ageing for three weeks, the specimens were tested in a Riehlé testing machine, upon an iron block drilled in the center with a 1-inch hole. Each test specimen

TABLE 9.

Results of Tests with Various Paints.

No.	Composition of Paints.	Results in Series I. 500-hour test.	Results in Series II. 300-hour test.	Series III Comparative bonding strength.
	Unpainted Blank Specimens.			
23.	Electrodes not painted.	Cracked at end of 240 hours. Passed large amount of current throughout test. Anodes badly corroded and pitted.	Cracked at end of 96 hours. Passed large amount of current throughout test. Anodes badly corroded and pitted.	2,010 lbs.
24.	Electrodes not painted.	Cracked at end of 50 hours. Same condition as No. 23.	Cracked at end of 96 hours. Same condition as No. 23.	2,750 lbs.
	Bituminous Paints.			
1.	Boiled, water-free coal tar, lime, Portland cement, and rosin, thinned with benzol.	No cracking shown. Passed only small amount of current. Some excretion of tar paint at anode.	No cracking shown. Passed only small amount of current.	1,530 lbs.
17.	Blown residual petroleum oil fluxed with gilsonite, dissolved in benzol and turpentine.	No cracking shown. Passed only small amount of current.	No cracking shown. Passed only small amount of current.	2,810 lbs.
	Aqueous Paints.			
4.	Silicate of soda, 40° Bé.	Cracked at end of 240 hours. Very little resistance to current.	Cracked at end of 168 hours. Very little resistance to current. Examination of iron showed some clear areas and some pitted.	700 lbs.
10.	Liquid glue.	Cracked at end of 240 hours. Passed large amount of current throughout test. Considerable iron hydrate at top of specimen and permeated throughout concrete around anode.	Cracked at end of 96 hours. Passed large amount of current. Dense deposit of iron hydrate at top of test piece. Bad corrosion of metal shown.	100 lbs.
11.	50% silicate of soda, 20° Bé., and 50% graphite ground together.	Cracked at end of 144 hours. Passed considerable current. Corrosion marked.	Cracked at end of 96 hours. Passed large amount of current. Corrosion marked.	Specimen faulty.
12.	50% silicate of soda, 20° Bé., and 50% iron oxide pigment ground together.	Cracked at end of 240 hours. Passed considerable current. Much corrosion.	Cracked at end of 192 hours. Passed considerable current. Much corrosion.	1,870 lbs.
19.	5% aqueous solution of sodium resinate.	Cracked at end of 144 hours. Passed more current than one blank specimen. Much rust.	Cracked at end of 144 hours. Passed considerable current. Much rust.	1,890 lbs.
20.	5% aqueous solution of sodium resinate ground with an equal weight of iron oxide.	Cracked at end of 240 hours. Passed large amount of current. Much rust.	Cracked at end of 196 hours. Passed large amount of current. Much rust.	2,580 lbs.

TABLE 9—Continued.

Results of Tests with Various Paints.

No.	COMPOSITION OF PAINTS.	RESULTS IN SERIES I. 500-hour test.	RESULTS IN SERIES II 300-hour test	Series III Comparative bonding strength.
OIL PAINTS.				
3.	Red lead in oil; 30 lbs. pigment to one gallon of raw linseed oil.	Did not crack, but large quantity of iron hydrate deposited at top surface of specimen, staining the concrete, showing weakened bond and corrosion.	Cracked at end of 192 hours. Considerable iron hydrate stain shown at surface of specimen throughout test. Iron quite badly corroded.	1,370 lbs.
13.	Chrome green 20% on 80% barytes base, ground in raw linseed oil (medium).	Cracked at end of 240 hours. Iron hydrate stain shown around anode at top surface of specimen early in test. Iron quite badly corroded.	Cracked at end of 192 hours. Same conditions observed as in Series I.	790 lbs.
14.	Blue lead in oil; 14 lbs. pigment to one gallon raw linseed oil.	No cracking shown. Resistance to current was not marked. Slight corrosion observed. Deposit of iron hydrate at surface of cylinder.	No cracking shown. Same conditions observed as in Series I.	1,250 lbs.
15.	Chromated iron oxide in oil; 12 lbs. pigment to one gallon raw linseed oil.	No cracking shown. Only slight corrosion observed.	Cracked at end of 144 hours. Deposit of iron oxide at top of cylinder.	930 lbs.
16.	Blue lead ground in heavy-bodied linseed oil reduced with an equal quantity of turpentine to cause paint to dry to a flat surface. Formed a thin film.	Small crack developed at end of 240 hours. No surface deposit shown, indicating good bond. Anode showed considerable corrosion.	Small crack developed at end of 216 hours. Same condition as in Series I.	1,400 lbs.
27.	Chromated iron oxide in treated tung oil; 12 lbs. pigment to one gallon raw linseed oil. "Sanded surface."	Not in Series I.	No cracking shown. Passed only small amount of current. No deposit on surface. Excellent condition.	2,000 lbs.
28.	Mixture of equal parts of No. 14 and No. 16. "Sanded surface."	Not in Series I.	No cracking shown.	1,880 lbs.
29.	Asbestine pigment ground in No. 9 oil. "Sanded surface."	Not in Series I.	No cracking shown. Passed only very small amount of current. Passed slightly more current than No. 9. In excellent condition throughout test.	Not in Series III.
OILS AND VARNISHES.				
2.	Special heat-treated tung-oil compound thinned with turpentine.	No cracking shown. Concrete test specimen was of faulty construction, a portion of the cathode being exposed. Nevertheless the specimen passed but very small amount of current. Film was tough and elastic.	No cracking shown. Only moderate amount of current passed. No stain.	2,665 lbs.

TABLE 9—Continued.

Results of Tests with Various Paints.

No.	COMPOSITION OF PAINTS.	RESULTS IN SERIES I. 500-hour test.	RESULTS IN SERIES II. 300-hour test.	Series III Comparative bonding strength.
5.	Double-boiled linseed oil (lead and manganese drier).	Cracked at end of 140 hours. Passed considerable current throughout test. Heavy deposit of iron stain at surface.	Only a very fine crack developed at end of test. Passed considerable current throughout test. No stain.	1,680 lbs.
6.	Kauri gum-linseed oil varnish.	Only slight crack shown. Small amount of current passed. No stain.	No cracking shown. No stain.	1,790 lbs.
9.	Processed tung-oil compound.	No cracking shown. Passed only a very small amount of current. Gave excellent insulation value. No stain.	No cracking shown. Passed only a very small amount of current. Had a high electrical resistance. No stain.	1,990 lbs.
22.	Mixture of equal parts of No. 9 and No. 21.	No cracking shown. Passed less current than No. 21, but more than No. 9. No stain.	No cracking. Passed less current than No. 21, but more than No. 9. No stain.	Specimen faulty.
LACQUERS.				
7.	Gum sandarac in alcohol; 32-oz. solution.	No cracking shown. Only small amount of current passed. No stain at surface.	Only small amount of current passed. No stain at surface.	990 lbs.
8.	Gum shellac in alcohol; 32-oz. solution.	No cracking shown. Passed more current than No. 7. No stain.	Passed more current than No. 7. Slight stain at surface.	490 lbs.
18.	Soluble nitrated cotton dissolved in amyl and ethyl acetates; 8-oz. solution.	Cracked at end of 240 hours. Large amount of current passed. Some stain at surface.	Cracked at end of 192 hours. Large amount of current passed. Iron hydrate stain at surface.	2,480 lbs.
21.	Gutta-percha dissolved in benzol; 3-oz. solution.	Cracked at end of 240 hours. Passed considerable current. Stain at surface.	Cracked at end of 96 hours. Passed considerable current. Considerable stain at surface.	2,600 lbs.
26.	Condensation product of phenol and formaldehyde dissolved in alcohol.	Not in Series I.	No cracking shown. Passed only small amount of current. Some iron stain at surface and a small deposit of dark cherry stain due to product of reaction between the phenolic bodies and the lime in the cement.	1,380 lbs.

was placed in such a position that the lower end of the contained iron anode would be in alignment with the hole below. Pressure was applied until the painted iron rod was pushed away from the surrounding cement and the bond destroyed.

OBSERVATIONS ON RESULTS.

In the test specimens, where cracking had occurred, the anodes showed considerable rust, the paint coatings originally applied having been destroyed. On the cathodes in Series I the paint coatings were still intact, although some had apparently been affected by the moisture and the hydrated lime in the wet concrete, chalky surfaces being shown. Wherever there were small voids in the concrete, at or around the painted anodes, corrosion was most severe, and at such places pitting was shown. The protective coatings upon the anode and cathode bars embedded in the concrete cylinders which did not crack and which carried but little current were later found to be in a very good state of preservation.

Incidental Reactions.—The breaking down of a film upon the embedded iron rods was always recorded by a sharp rise in the amperage, due to the decreased resistance offered to the flow of the current between the electrodes. It was also recorded by a fizzing sound, due to the increased evolution of hydrogen gas developed by the electrolysis of the water in the damp concrete. This gas, issuing from around the iron electrode at the top of the test pieces, generally carried some water with it, and small bubbles were formed, which burst with an audible explosion when a lighted match was placed in contact with them. The hydrogen gas seemed to have a reducing or softening action upon some of the oxidized coatings and carried to the surfaces of the cylinders considerable quantities of soft, oily products, which deposited around the anode and later hardened in contact with the air. Iron oxide was also carried to the top surfaces of some of the specimens by the action of the gas and water and was there deposited as a dark brown stain.

Electrolytic Hydrogenation of Oil Films.—That the nature of the paint films has considerable bearing upon the action of the hydrogen gas which was found to be developed during the tests, there can be no doubt. In an investigation to determine the cause of the rapid corrosion exhibited by some grades of lacquered tin food containers, W. H. Walker* and Slade† have found linseed-oil films to act as depolarizers of hydrogen, and Walker points out that such films, if in a semi-

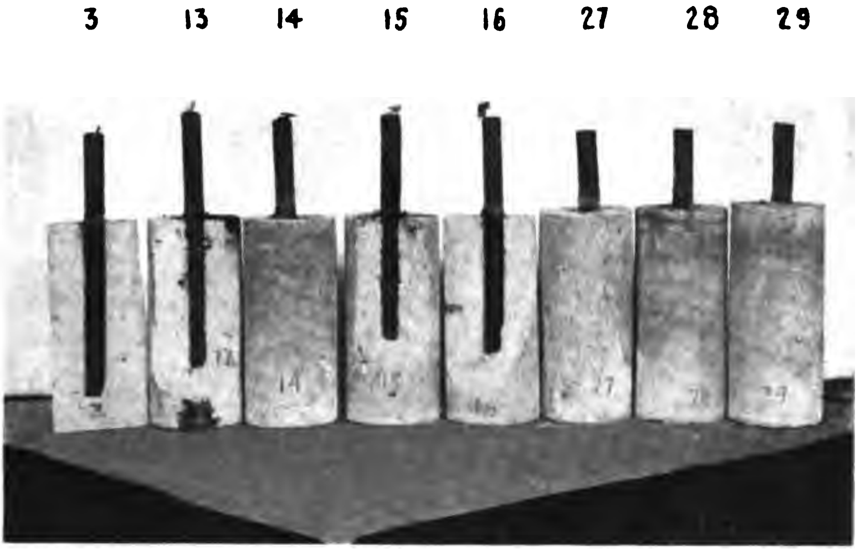

Fig. 43.

Part of Test Cylinders—Series II.

Nos. 3, 13, 14, 15, 16, 27, 28, 29 contain rods coated with various oil-pigment paints. Note excellent condition of 27, 28, and 29, which contain "sanded" painted rods.

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*"Paint and Varnish Coatings as Accelerators in the Corrosion of Metals," W. H. Walker and W. K. Lewis, J. Indus. and Engrg. Chem., 1 (1909), 754.

†"A New Method for Testing Paint Films and Preservative Coatings for Iron and Steel," W. C. Slade, *Ibid.*, 4 (1912), 189.

oxidized condition, may absorb hydrogen quite as rapidly as oxygen. This may account for the appearance of the oily substances brought to the top of some of the cylinders. Electrolytic hydrogenation may have been effected by the action of the nascent hydrogen in the presence of iron oxide or other pigments which could act as catalyzers. The action was sufficient to produce a product which, although fluid when formed, on account of the warmth of the cylinders at the anode where heat was developed by the electrolysis, later became solid when deposited upon the surface of the cylinders. It was in specimens showing such surface deposits that the bond between the cement and steel was the weakest.

Value of Well-dried and Saturated Films.—Walker has also referred to the fact that paint films that have been baked do not act as depolarizers, on account of their fully saturated condition. It would obviously be impractical to bake paint coatings upon most forms of reinforcing metal, but quite thoroughly oxidized coatings, which would probably have but slight depolarizing action, would result by allowing a period of sixty days for the drying of oil paints after application to the metal and previous to immersion in the cement. It is, moreover, possible to apply coatings which do not depend entirely upon oxygen absorption for their hardening and which contain ingredients of a fairly saturated nature. Among these could be mentioned such coatings as are composed of resins dissolved in volatile solvents, as well as some special types of oil coatings which gave good results in Series I and II.

Relation Between Film Porosity and Electrolysis.—The small current flow shown by certain of the specimens in the test may in part be attributed to their impervious character. Paints which form porous films allow the passage of water which may contain various electrolytes. Such films offer but small resistance to the passage of electrical currents. Paints which form highly impermeable films keep water away from the underlying iron and offer great resistance to the passage of electrical currents. Investigations which have determined the actual degree of porosity shown by various types of paint films have previously been made by A. M. Mucken-

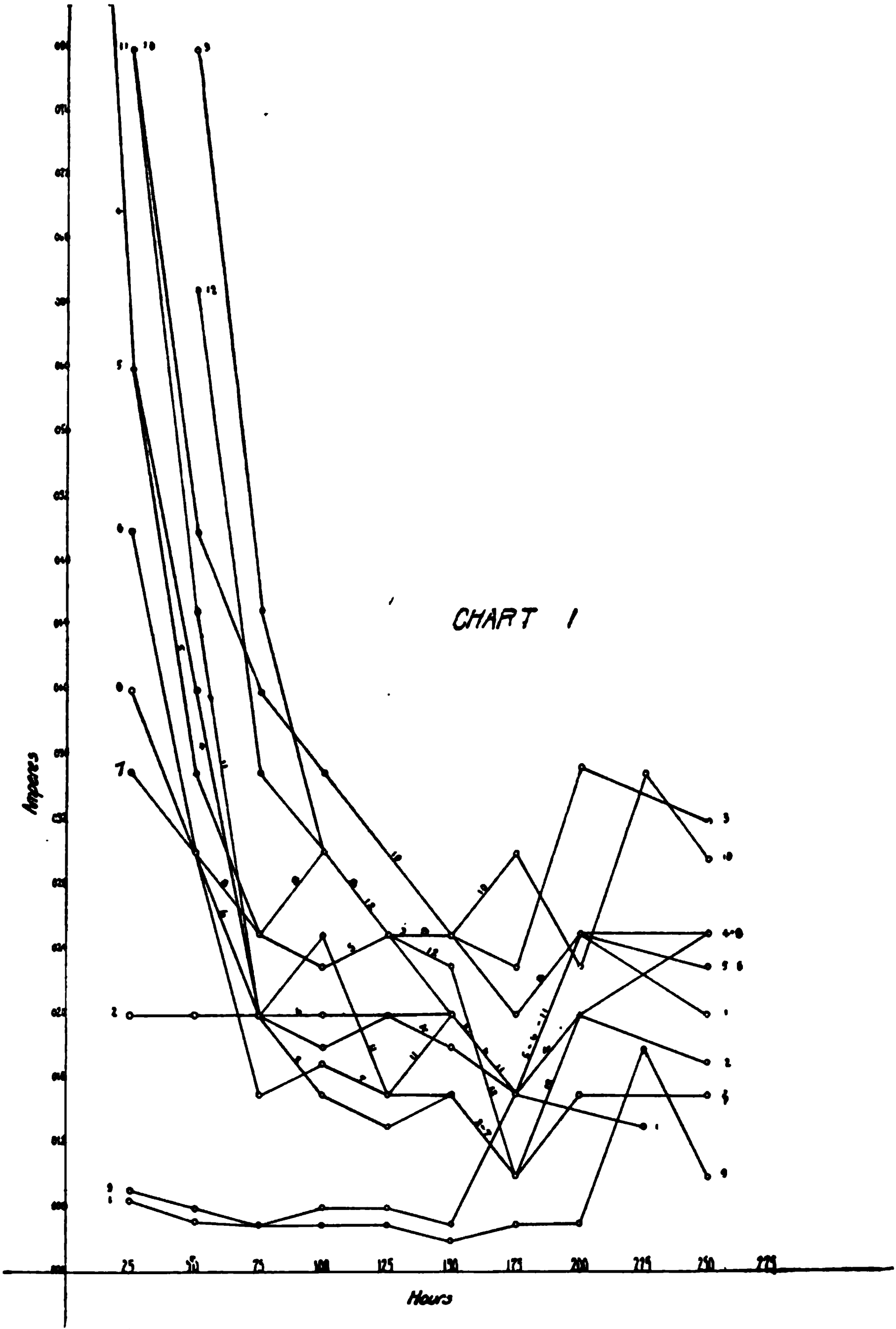

DIAGRAM II—AMPERE-HOUR CHART I FOR SERIES II.

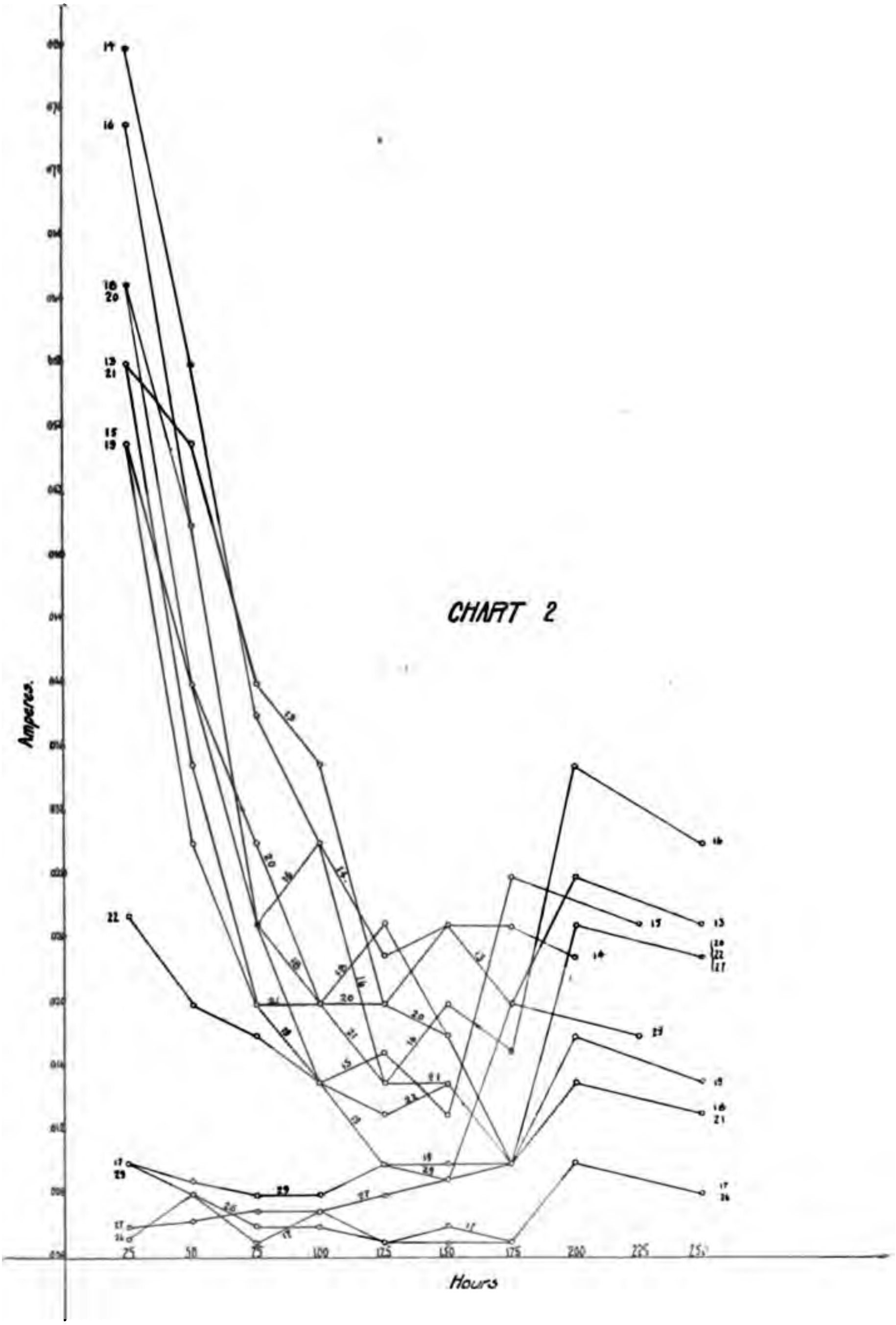

DIAGRAM II (CONTINUED)—AMPERE-HOUR CHART 2 FOR SERIES II.

fuss* and by the writer.† These tests have already afforded useful information to the designer of paints and might be studied with profit in the production of paints for the prevention of electrolytic corrosion.

Bonding Tests.—Some paints gave good bonding tests, but failed to act as insulators. Among these may be mentioned Nos. 12, 19 and 20 (water paints) and Nos. 18 and 21 (lacquers). The latter two, composed of collodion and gutta-percha, respectively, dried to a flat surface which accounts for the good bond tests shown. Among the oil paints, No. 16, which also had the property of drying to a flat surface, gave a much better bond than paints of a similar composition which dried to a gloss surface. The good bonding tests shown by several of the water paints is readily explainable, the wet concrete exerting a solvent action upon such paints, which gave opportunity for direct contact with the steel. Some paints which gave excellent results in the insulating tests gave conversely poor results in the bonding tests. Among these may be mentioned Nos. 7 and 8, composed of sandarac and shellac, respectively. Most of the oil-pigment paints made with raw linseed oil gave poor or only fair results. It is probable that the raw oil fails to dry hard, and, although apparently well dried, remains in a semi-oxidized condition. The oil films would in such cases be rather porous and therefore inefficient as insulators. Such films would be readily acted upon by the hydrogen evolved by electrolysis. Much better results were obtained with boiled linseed oil, a product that dries to a harder, less porous, and more fully saturated film. The value of the "sanded surface" method is shown by comparing test No. 27 with test No. 15, the paints used being of the same composition. The sanded surface of No. 27 gave much better insulating values and its bonding strength was double that of the unsanded specimen. Another instance of the value of the "sanded surface" method is shown by a comparison of specimens Nos. 28 and 14.

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*"Report on a Permeability Test for Paints and Varnishes." A. M. Muckenfuss, Journal Indus. and Engrg. Chem., 5 (1913), 535; Proc. Amer. Soc. for Test. Mater., 14, II (1914), 361.

† "Excluding and Water-resisting Properties of Paint Films for the Protection of Iron and Steel," H. A. Gardner, Bull. 18, Scientific Section, Paint Mfrs. Assn. of U. S., p. 17.

Use of Pigments.—It is quite likely that the nature of the pigment used in a paint designed to prevent electrolysis of embedded metal will have some bearing upon the results obtained from its use. The addition of a pigment to an oil usually increases the resistance to moisture and makes a more impermeable film. Theoretically, pigments which are of a non-conducting nature should be preferable. The inert pigments are examples of this type (asbestine, china clay, silica, etc.). There should, however, be present in a paint a sufficient quantity of rust-inhibitive pigment (basic pigments or pigments of the chromate type) to produce a passive condition of the steel, similar to the condition that is produced by the basic lime compounds in cement.

Prominent among the protective compounds that gave the best results are Nos. 2 and 9, composed of processed and heat-treated tung oil (Chinese wood oil). These compounds dried to a hard, non-porous film of a saturated nature. Had they been sanded, they undoubtedly would have given still better results. Distinction should also be accorded to Nos. 17, 27 and 28, although the good results obtained with the last two should be largely credited to the sanding of the surfaces during drying.

CONCLUSIONS.

The corrosion of metal embedded in concrete structures, by stray currents of high voltage, is often productive of serious effects. The use of properly made paints upon such metal constitutes a safeguard that should not be neglected by the engineer. Such paints may be prepared as follows:

I—The vehicle should contain:
  1—Boiled or bodied oils or products which dry to fairly saturated films.
  2—Oils which dry by semi-polymerization rather than by oxidation.
  3—Oils which dry to a flat rather than a high gloss surface.

II—The solid portion should contain a percentage of:
  1—Pigments which are coarse and which therefore tend to form films having a rough surface.
  2—Pigments which are inert and which do not act as conductors of electricity.
  3—Pigments which are either basic or of the chromate type.
III—The painted metal should be "sanded" if possible.

CHAPTER VIII.

PAINTS FOR METAL.

Metal Primer Tests.—A series of tests to determine the efficiency of basic pigments as primers for metal were exposed in May, 1914, at Washington. The object of the tests was to ascertain whether red lead of high or low basicity is best suited for protecting metal from corrosion. Other pigments which are known to be good metal protectives were included in the tests, in order to have a definite standard upon which to base the service of the red leads.

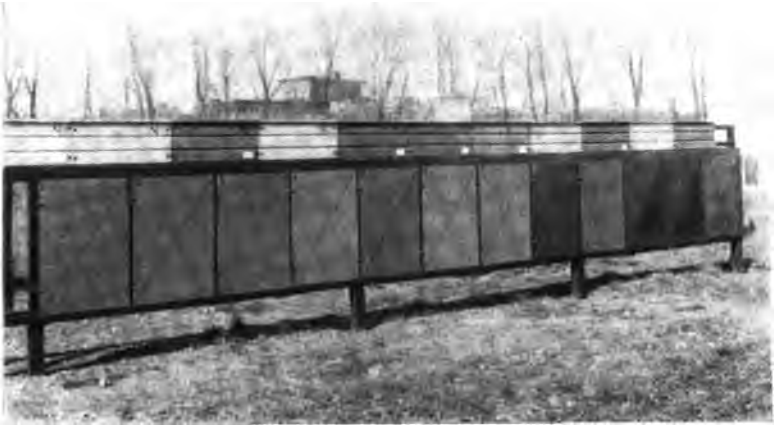

FIG. 44.

The paints were all applied to the same grade of black iron plates free from rust. The first coat of each paint was applied to the entire surface of the plate at a spreading rate of 600 square feet per gallon. The second coat was applied only to the lower right-hand half of the plate, at a spreading rate of 900 square feet per gallon. Four days were allowed for drying between coats. The paints were all applied to the panels after they had been attached to the supporting fence frame. The red lead paints were prepared so that they would all be of the same viscosity or body. The standard formula of 25 pounds dry pigment to 1 gallon of oil was found practical except with pigments 6 and 7, which required more oil to bring them to working consistency and to the same viscosity as the others.

The composition of the paints applied is given in the following table:

TABLE 10.

Panel No.	Pigment	Grade (Lead Tetroxide Content)	Pigment in Paint	Linseed Oil in Paint	Weight per Gallon. Lbs.
1	Red Lead.....	86%*..........	80	20	27
2	" "	88%*..........	80	20	25
3	" "	90%*..........	79	21	28
4	" "	93%*..........	78	22	24
5	" "	95%*..........	80	20	27
6	" "	99%*..........	72	28	21
7	" "	Special**.......			
8	Sublimed Blue Lead.	Contains 1% added carbon black	63	37	16½
9	Chromated Red	Contains 2% CrO_3	76	24	22
	Lead.	Contains 1% CrO_3	56	44	14
10	Chromated Iron Oxide.	10% Zinc Chromate.	55	45	14½
11	Iron Oxide K..	Contains 20% Zinc Oxide.			
12	" " H..		58	42	15

*Balance is litharge.

**Special Red Lead purchased in paste form.

Results of tests: Photographs (Figs. 45 and 46) taken during the first two years' exposure show the condition of some of the panels.

No. 1. 86% Red Lead. No. 2. 88% Red Lead. No. 3. 90% Red Lead. No. 4. 93% Red Lead. No. 5. 95% Red Lead.
Nos. 6 and 7. 99% Red Lead.

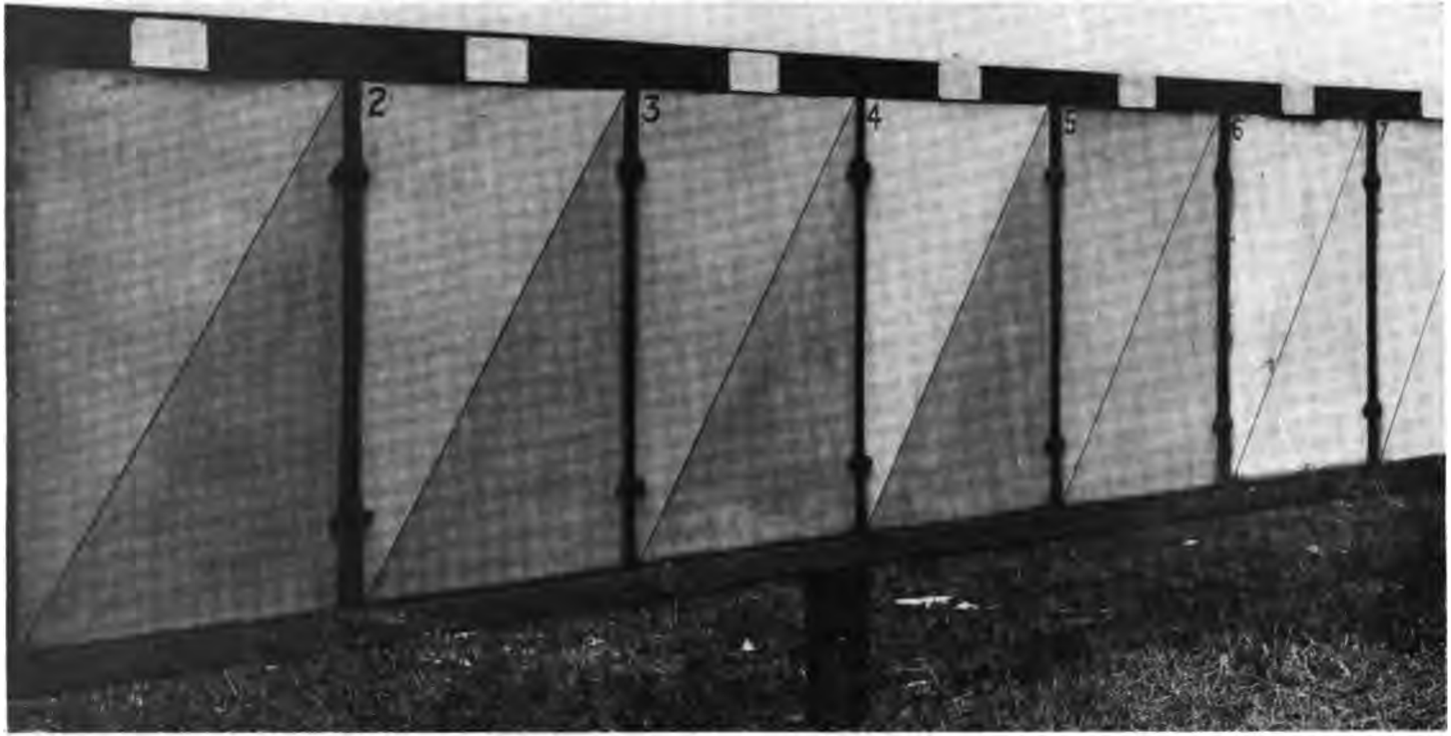

FIG. 45.

RED LEAD PRIMER TESTS ON METAL PLATES. Exposed May, 1914.

Upper portion of each plate one-coat work. Lower portion two-coat work. Light color shown by plates 4, 5, 6, and 7 due to disintegration of surface film and formation of lead carbonate through reaction with carbon dioxide present in the air.

Panels 1, 2, and 3 are in the best condition, corrosion being absent and original red color of paint retained.

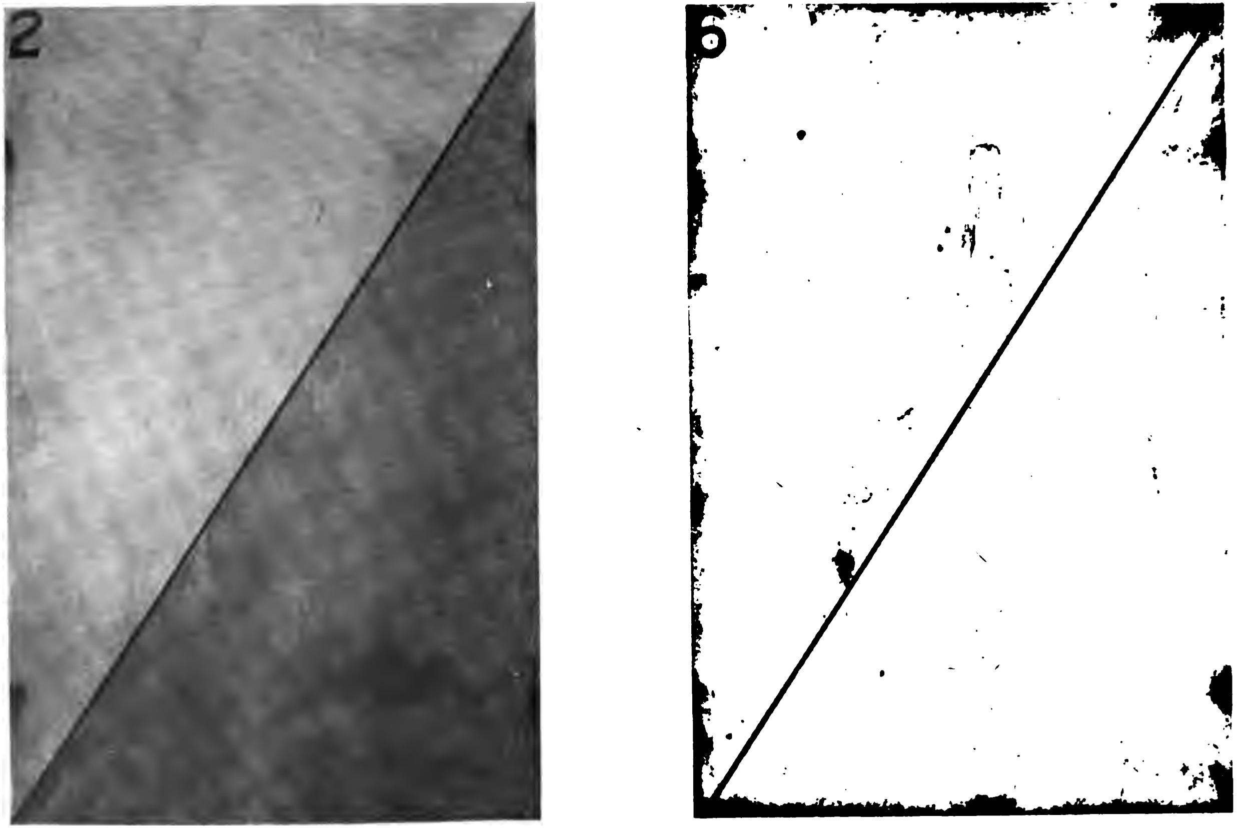

FIG. 46.

VIEW TAKEN AFTER TWENTY MONTHS' EXPOSURE.

DETAIL VIEW OF PANEL NO. 2.
88% Red Lead.
12% Litharge.

DETAIL VIEW OF PANEL NO. 6.
99% Red Lead.
1% Litharge.

Note how Panel 6 has faded and corroded, especially at edges.

Prepared Paints for Metal Surfaces.—In designing protective coatings for metal the modern practice has been to apply the results available from researches into the cause of corrosion. These results have shown that materials of a basic nature or substances which contain soluble chromates prevent the rusting of iron. For this reason pigments of a basic nature or pigments containing the chromate radical have come into wide use in the manufacture of protective paints. That they are the best pigments for this purpose has been proved not only in practice, but also in the Atlantic City tests,* which were made upon a series of three hundred large steel panels, using nearly one hundred different pigment paints. Applying the results of these tests to the practical manufacture of protective coatings, the writer will discuss the use of the vari-

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* As a final summing up of these most authoritative tests to determine the value of different pigments in protecting metal, the following table is presented. This shows the pigment paints which rated highest at the various annual inspections.

This table does not show pigments which were not included in the ten highest classes. For full description of tests and further information see Proc. Amer. Soc. for Test. Mater., Vol. IX, 1909, pp. 203 and 204; Vol. X, 1910, pp. 79-86; Vol. XI, 1911, pp. 192-194; Vol. XIII, 1913, pp. 369-371; Vol. XIV, 1914, pp. 259 and 260.

TABLE II.

Pigment Paints of Ten Highest Average Ratings, 1910-1914

	1910	1911	1912	1913	1914
Basic chromate of lead	9.1	10.0	9.9	9.8	7.5
Sublimed blue lead	9.6	8.8	9.0	7.2	6.0
Carbon black and barytes	....	....	....	6.8	5.0
Chrome green	9.8	9.8	8.6	7.6	5.0
Willow charcoal	....	8.8	8.6	7.9	4.5
Red lead	....	....	8.1	....	4.0
Natural graphite, containing clay, etc.	....	....	....	....	4.0
Zinc chromate	9.4	9.5	8.8	8.0	4.0
Zinc-and-lead chromate	9.5	9.7	9.2	8.3	4.0
Magnetic black oxide	9.5	9.5	8.6	7.8	4.0
Zinc-and-barium chromate	9.7	9.5	8.5	7.8	....
Sublimed white lead	9.5	9.0	8.1	....	....
Bright red oxide	9.3	....	....	....	....
Prussian blue (water stim.)	9.2	....	....	6.7	....
Prussian blue (water inhib.)	....	8.5	....	....	....

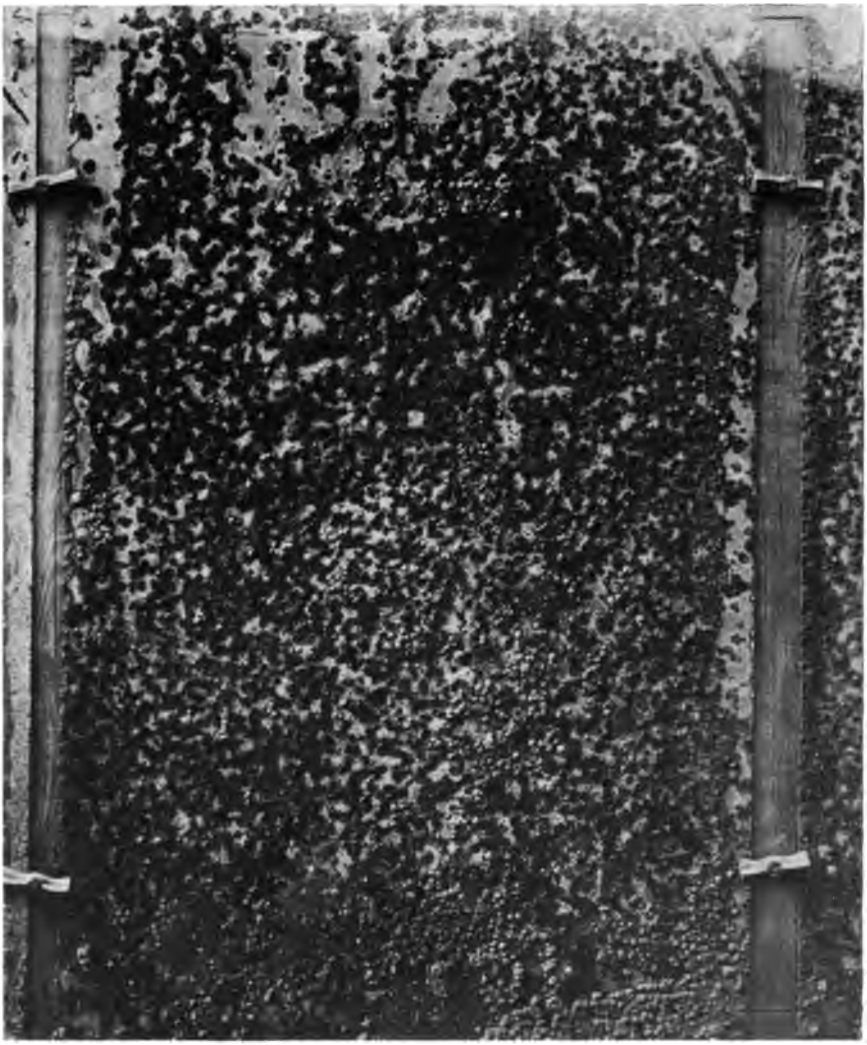

FIG. 47.

Steel panel painted with graphite (rust stimulative) paint, after eight years' exposure. Paint applied direct to metal surface.

ous pigments under separate headings, taking up the composition of the most widely used colors for metal painting, namely, red, gray, black, and green. Most of the paints outlined herewith are suitable for the painting of structural steel, bridges, steel railroad cars and equipment, ornamental ironwork, poles, posts, and for general work on metal surfaces.

Red-Lead Priming Paints.—Red lead may be purchased in the market ground to a heavy paste in linseed oil, ready to thin with oil for use. Such red lead is usually produced by the thorough oxidation or overburning of lead, the dry pigment generally containing approximately 98% of lead tetroxide. This pigment, being practically free from litharge, is supposed not to react to any great extent upon the linseed oil in which it is ground. It is well understood, however, that one of the most valuable properties of red lead is its ability to set up to a hard, elastic film that shuts out moisture and gases which are apt to cause corrosion. This cementing action is due to the presence of unburnt litharge, a pigment which rapidly reacts upon linseed oil to form a lead linoleate compound. It will readily be seen, therefore, that red lead free from litharge has no cementing action and should not be considered more protective than iron oxide or any other similar neutral pigment. It is thoroughly essential that red lead should be highly basic and should contain a considerable percentage of litharge, if the red lead is to protect iron from corrosion. Although such red lead is often purchased in the dry form and mixed with linseed oil on the job at the time of application, it is a growing custom to use prepared red-lead paints made from finely divided red lead ground to a fluid condition in linseed oil. Such paints remain in excellent condition for a long period of time. They have a high protective value and are well suited for general purposes. They are used extensively for priming steel vessels. The Navy Department has found that inert pigments, such as silica and asbestine, give good results when used in ready mixed red-lead paints, their action being to prevent settling of the red lead upon storage.

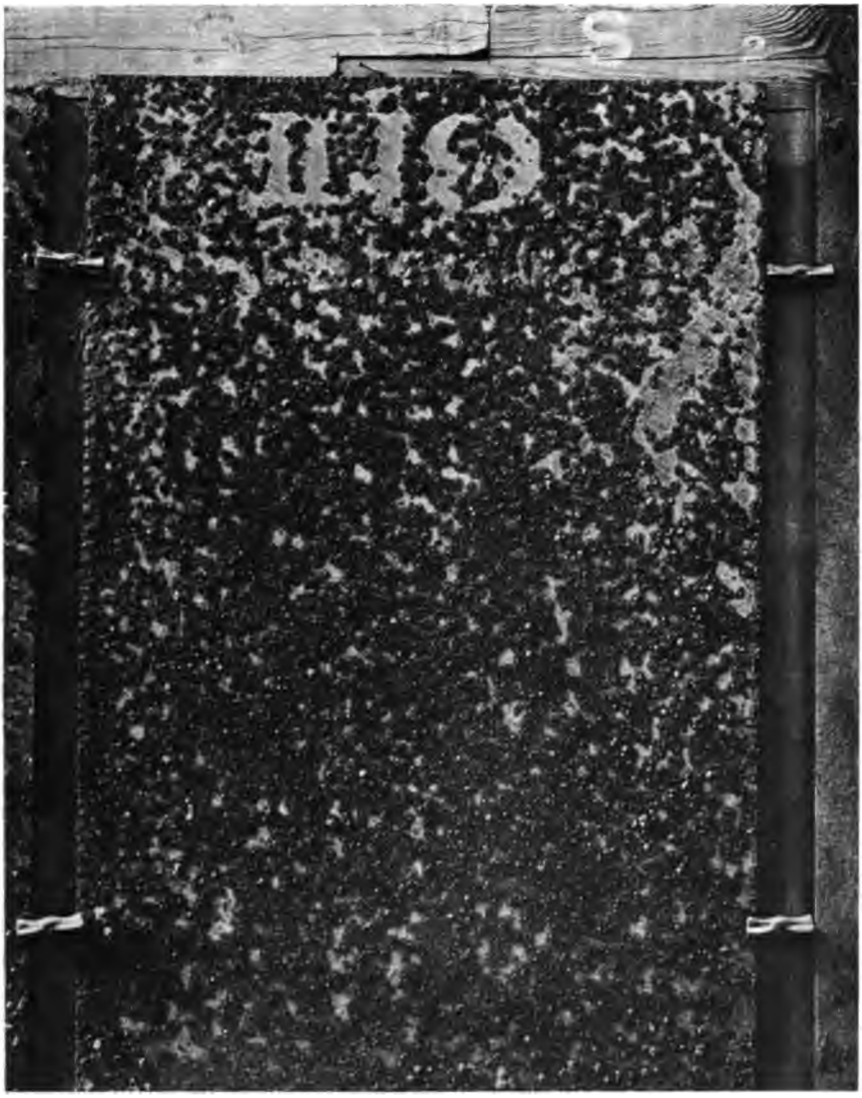

Fig. 48.

Steel panel painted with carbon (rust stimulative) paint, after eight years' exposure. Paint applied direct to metal surface.

A specification which may be used by the grinder when purchasing dry red lead for the manufacture of prepared paints is given herewith:

Specification.

1. The dry pigment to be of the best quality, free from all adulterants, and to contain not less than 85% nor more than 90% Pb_3O_4, the remainder being practically pure lead monoxide (PbO).

FIG. 49.

Tests exposed by the writer on Young's Ocean Pier, Atlantic City, N. J. Reported on by Com. D. 1, A. S. T. M.

2. It shall contain not more than 0.1% of metallic lead nor more than 0.1% of alkali figured as Na_2O.

3. It shall be of such fineness that not more than 0.5% remains after washing with water through a No. 21 silk bolting-cloth sieve.

NOTE.—If desired, the gram weight of the red lead may be specified. Extremely light, fluffy red lead should run from 10 to 13 grams per cubic inch. Medium red lead will run from 13 to 16 grams per cubic inch. Heavy red lead will run from 17 to 19 grams per cubic inch.

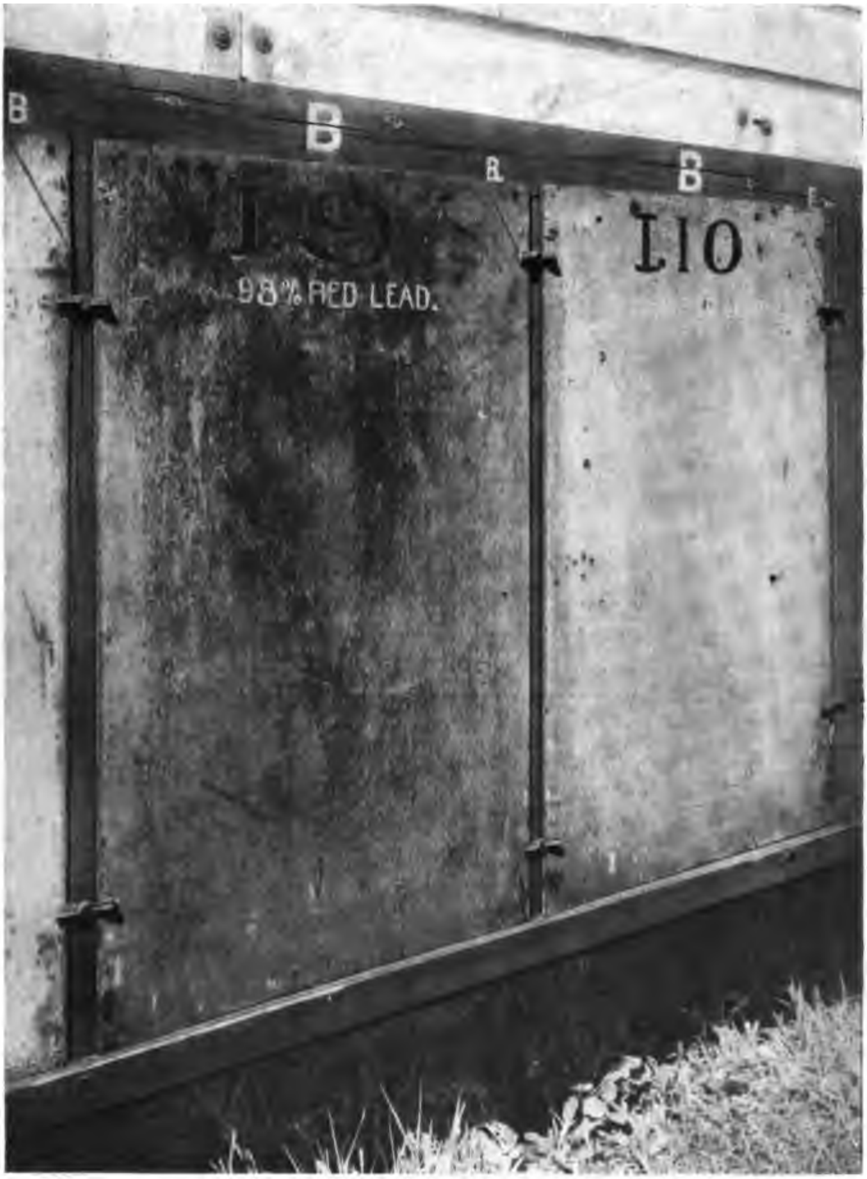

FIG. 50.

Test of 98% and 85% Red Leads. Panels from Atlantic City Test Fence. Exposure, eight years.

Composition of Red-Lead Priming Paints.—The cost of red-lead paints is a subject of vital importance to the large user. Red lead may be produced in different physical states. Ordinarily the grade that has been overburned is extremely heavy, one cubic inch weighing from 18 to 20 grams. For the production of a paint from such red lead, according to the formula used by one large consumer, the following quantities would be required:

Red lead	26 lbs.
Linseed oil	26 gills
Petroleum spirits	3 "
Drier	3 "

This would produce approximately 1 2/5 gals. of paint. Each gallon would contain about 20 lbs. of red lead, the actual cost of the red lead itself being in the neighborhood of $1.60.* A red lead of a much better protective value, containing from 10 to 12% of free litharge and produced in an extremely fine physical state of comminution, so that one cubic inch would not weigh over 12 to 15 grams, would produce a paint of exactly the same body on the following formula:

Red lead	20 lbs.
Raw linseed oil	26 gills
Turpentine	3 "
Drier	3 "

This would produce approximately 1 1/3 gals. of paint, each gallon of which would contain about 15 lbs. of red lead, the actual cost of the dry pigment per gallon being in the neighborhood of $1.20. Red lead of still lighter gram weight could be used, so that a still smaller quantity of pigment would be required per gallon of oil. The durability of such paints should compare favorably with those containing very high percentages of red lead of high gram weight. Pigments of an extremely light nature, such as lampblack, grind in very

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* Figured with red lead at 8 cents in 1914.

Fig. 51.

Appearance of steel panel coated with high-grade rust-inhibitive paint, made of Basic Chromate of Lead.

large quantities of oil, yet their films are more elastic and durable than many paints which are composed of much pigment and little oil.

Red Paints.—Iron oxide has always been one of the most widely used pigments for the manufacture of protective coatings. Oxides that are free from acid or soluble substances give the best results. There are many grades, from the brilliant Indian reds, containing 98%, down to the natural mined brown shale oxides, containing from 30 to 60% of ferric oxide, the balance being silica, clay, etc. Venetian reds, consisting of about equal parts of ferric oxide and calcium sulphate, are also quite widely used. It is customary to add to iron oxides from 10 to 20% of zinc chromate, zinc oxide, or red lead, in order to make them rust inhibitive. Such red paints are widely used for application to tin roofs, metal siding, and general structural steel. Red paints made from basic lead chromate (American Vermilion), the pigment which gave the best results in the Atlantic City tests, would doubtless be the most economical in the long run, but the high cost will probably prevent their use to any great extent. The use of a percentage of basic chromate of lead in iron-oxide paints is to be approved.

Gray Paints.—Mixtures of white lead (basic carbonate or basic sulphate) and zinc oxide, tinted gray with carbon black, are widely used for this purpose and give excellent results in every climate.

A valuable rust-inhibitive coating for general priming or finishing work may be prepared from sublimed blue lead. The use of two parts of blue lead and one part of linseed oil containing about 5% of turpentine drier makes a paint of the right consistency. This may be purchased in prepared form. When this paint is used for top-coat work in marine exposures (battleship gray), the addition of 1% of carbon black to the blue lead aids in the maintenance of the color. The rust-inhibitive value of this pigment is due to the high percentage of lead oxide (litharge). This pigment, however, is so combined with the lead sulphate that it does not have any great hardening action upon the linseed oil and

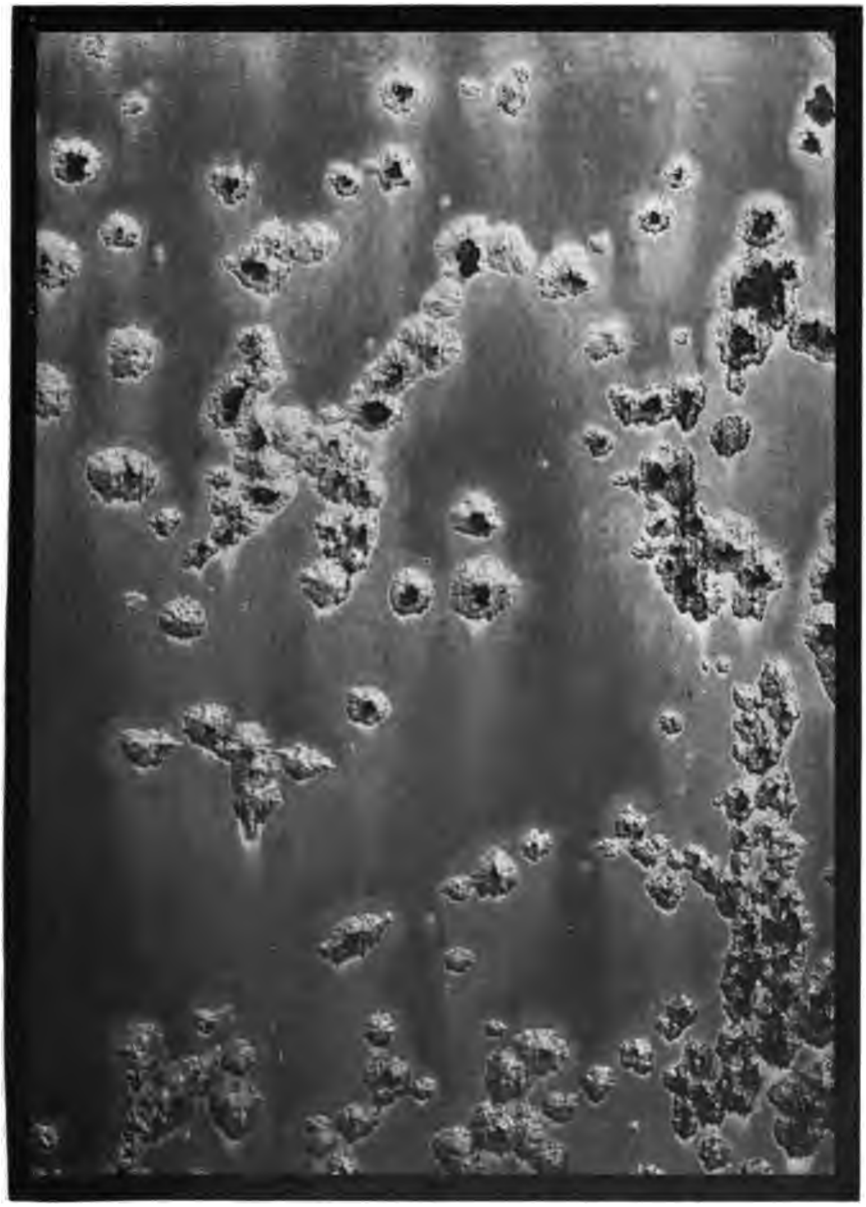


FIG. 52.

Appearance of steel panel coated with improperly prepared paint containing a rust-exciting pigment.

stays in an excellent condition in paste form for a long period of time without hardening. When purchased ground to a paste in 10 parts of oil, there should be added approximately 5 gallons of linseed oil and one pint of drier for use. A specification for the purchase of blue lead for use in metallic paints is given herewith:

	Minimum.	Maximum.
Lead sulphate	44%	52%
" oxide	33%	40%
" sulphide		0.5%
" sulphite		3.5%
Zinc oxide		3.0%

Black Paints.—Black paints are often preferred for the finishing coat on steel work, carbonaceous paints being unsuited for application direct to the metal on account of their rust-stimulative action. Carbon pigments, such as gas carbon black, oil black, artificial and natural graphite (flake and amorphous) are usually the base pigments used in black paints. Silica and other earth pigments may be combined with the carbon. The slow-drying nature of such paints is lessened by the addition of litharge. The use of boiled linseed oil as a vehicle is advisable.

Magnetic black oxide of iron (precipitated) forms an excellent black protective paint when ground in linseed oil. The slightly basic character of this pigment accounts for its inhibitive value. The natural variety of black magnetic oxide of iron is also suitable for this purpose, but should be tested for freedom from soluble acid impurities before use. Willow charcoal is not made in commercial quantity; its use, therefore, will be restricted. Its inhibitive value depends upon the basic nature of the impurities present.

Green Paints.—Mixtures of zinc chromate and Prussian blue in oil are highly inhibitive and have proved satisfactory in long service tests. Chrome yellow tinted with black oxide of iron to an olive shade is very permanent and protective. Chrome green made from lead chromate and Prussian blue is generally used when precipitated upon a barytes base.

Bituminous Paints.—Bituminous coatings have a wide use for special purposes. They are often made by blending refined coal-tar pitch, asphalt, linseed oil, and oleo-resinous varnishes, subsequently thinning down with turpentine or light mineral thinner. During recent years a heavy-bodied blown petroleum residual pitch has come into wide use in the manufacture of waterproofing bituminous paints. This pitch usually has a high melting point (150° C.). It is soluble in turpentine, benzol, and some mineral distillates. When in solution it may be admixed with oils for the production of rapid-drying elastic paints. The pitch has high resistance to acids and is not acted upon by the sun to the extent that coal tar is.

When coal tar is used in the manufacture of paints, it should be refined. Ammonia and water in the tar are the active causes of saponification or non-adherence to metal. The presence of large quantities of free carbon or naphthalene in the tar will cause disintegration and checking. For refining, the crude tar may be heated to approximately 115° C., holding it at that temperature until the water is evaporated. From 5 to 10% of lime may be stirred in, in order to neutralize the free acids. The tar may then be thinned with benzol or mineral spirits. If a rapid-drying paint is desired, a quantity of resinous varnish may be added. The addition of Chinese wood oil and asbestine in a coal-tar paint made along the above lines will aid in producing a film that is not so subject to alligatoring when exposed to the sun.

Bituminous paints of the above composition are used as coatings upon pipe-lines in acid factories, tanks containing dilute acids, metal submerged in water, and for other similar work. For such purposes it is generally advisable to first coat the metal with a thoroughly hard drying prime coating made by adding 2 lbs. of litharge to a prepared red lead or other rust-inhibitive paint. The bituminous paint may then be applied. Steel mine timbers subjected to sulphur water and gas reservoir tanks containing water, submerged lock gates, tunnel metal, etc., may be efficiently preserved from corrosion by this method.

Painting Galvanized Iron.—Metallic zinc is the most valuable metal, from an economical standpoint, that may be used as a protective coating on iron and steel. Moreover, it is capable of producing by various processes (Hot Dip, Vapor, and Electro-Galvanizing) a continnuous film which is highly protective. It must be understood, however, that its ability to prevent iron from rusting is accomplished at its own

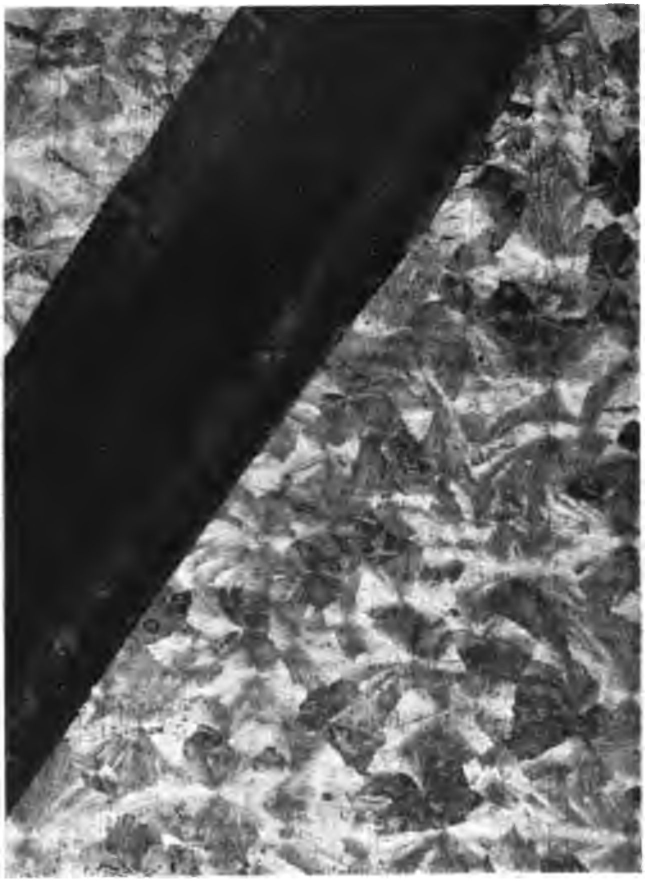


FIG. 53.

The black stripe on the sheet of galvanized iron is produced by brushing on a solution of copper salts. This treatment prepares the metal to receive and hold paint coatings.

expense, the zinc gradually disappearing as exposure to the weather continues. For this reason, and for the purpose of decoration, it is customary to paint articles made of galvanized iron, such as roofing, siding, railings, drain pipes, cornice work, etc. The smooth, spangled surface which is shown by many of these articles will unfortunately tend to prevent the adherence of even the best paints, and peeling may ultimately result. This condition, however, is obviated by first treating the galvanized iron before painting with a solution of copper salts, which may be prepared by dissolving 4 ounces of the chloride, acetate, or sulphate of copper in one gallon of water. By brushing on this solution the galvanized iron is roughened, a thin deposit of copper being plated out over the surface. After an hour or so the surface may be dusted off and then painted with a prepared metal paint. Red, white,

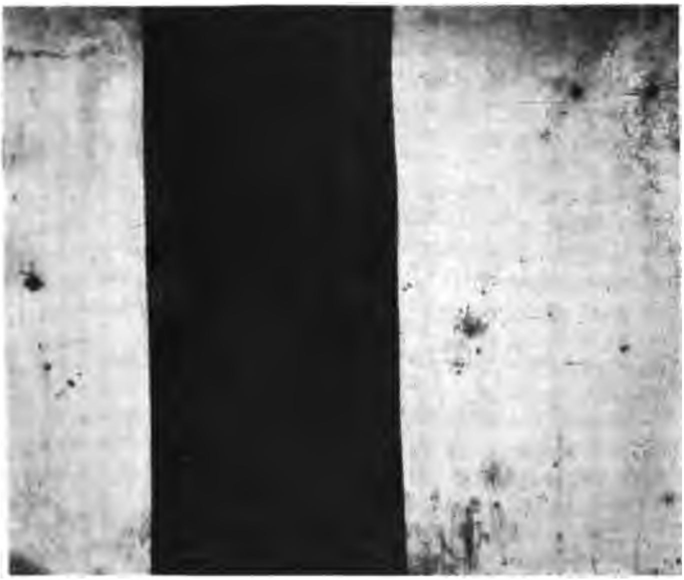


FIG. 54.

A sheet of heavily coated tin plate was exposed to the weather after painting a stripe across the middle section. In a short time the unpainted section developed many rust spots at pin-holes in the tin coating.

and blue leads; zinc oxide and chromate pigments; red and black iron oxides, and inert pigments are constituents of the higher grade prepared paints for priming or finishing metal surfaces. Such paints are also suited for use on metal shingles and pressed steel siding—black, galvanized, or tinned. Carbon paints are used only as finishing coats.

Painting Tinned Surfaces.—Tin plate, such as is used for roofing and siding, will rapidly corrode unless coated with paint. Even the very best grades of heavily coated tin plate are subject to pin-holing, as it is practically impossible to uniformly coat the surface of iron with molten tin without leaving occasional imperfections which expose the base metal. These places furnish points of attack, serving as pockets to catch moisture which causes the formation of rapidly developing rust spots. It is therefore good practice to paint tinned surfaces within a day or two after placement. Before applying paint to the tin, it is advisable to rub the surface of the sheets with cotton waste saturated with benzine or turpentine. This treatment will remove the palm oil that may be present on the surface and allow the paint to firmly adhere. Red iron oxide paints in prepared form, containing an inhibitive pigment, are widely used for preserving tin. The use of 15% to 20% of red lead, zinc oxide, or zinc chromate with a neutral bright iron oxide produces an excellent grade of paint. The partial use of boiled linseed oil or kauri gum varnish will add to the gloss and water resistance. For dipping purposes, turpentine or high boiling-point mineral spirits should be used for thinning. The use of driers containing a low boiling-point benzine should be avoided.

CHAPTER IX.

MARINE PAINTS.

One hundred tons of paint, costing approximately $25,000, represents the initial color requirements of a new battleship. The annual upkeep cost may even exceed this sum, since it is the custom to repaint different parts of a modern war vessel every three to six months. This would indicate an annual paint protection outlay of nearly a million dollars for our Navy. If to this sum we should add the cost of painting the thousands of lake boats, freighters, river steamers, and pleasure craft, a conception may be had of the importance of marine paints. While many different types of painting products are used on vessels, only those which find the most universal application will be discussed in the following paragraphs.

Primer Paints.—The priming coat of paint upon steel vessels is the most important of all, since protection from corrosion is governed by the effect of the initial coating applied to the steel. Many thousand tons of red-lead paint are annually used for this purpose. At the present time most red-lead paints that are used for naval vessels come in prepared form ready for brushing, one of the most satisfactory being composed of two parts of red lead and one part of silica, ground in linseed oil, drier, and mineral spirits. Such a paint, if well made, will remain in prepared form in a can for a long period of time without showing any tendency to harden, even though the red lead should contain up to 12% of litharge.

Bottom Paints.—Among the most important naval paints are those which are applied to protect the submerged parts of the hulls from corrosion or fouling by barnacles. The word "barnacle" is the popular name for that form of marine crustacea of the order *Cirripedia*, which consists of a clamlike body lodged in a shell that is often formed in a series of rings or plates. They become attached and adhere with great tenacity to rocks, pilings, and vessels. When removed from a ship's bottom, the clamlike body will be found separated

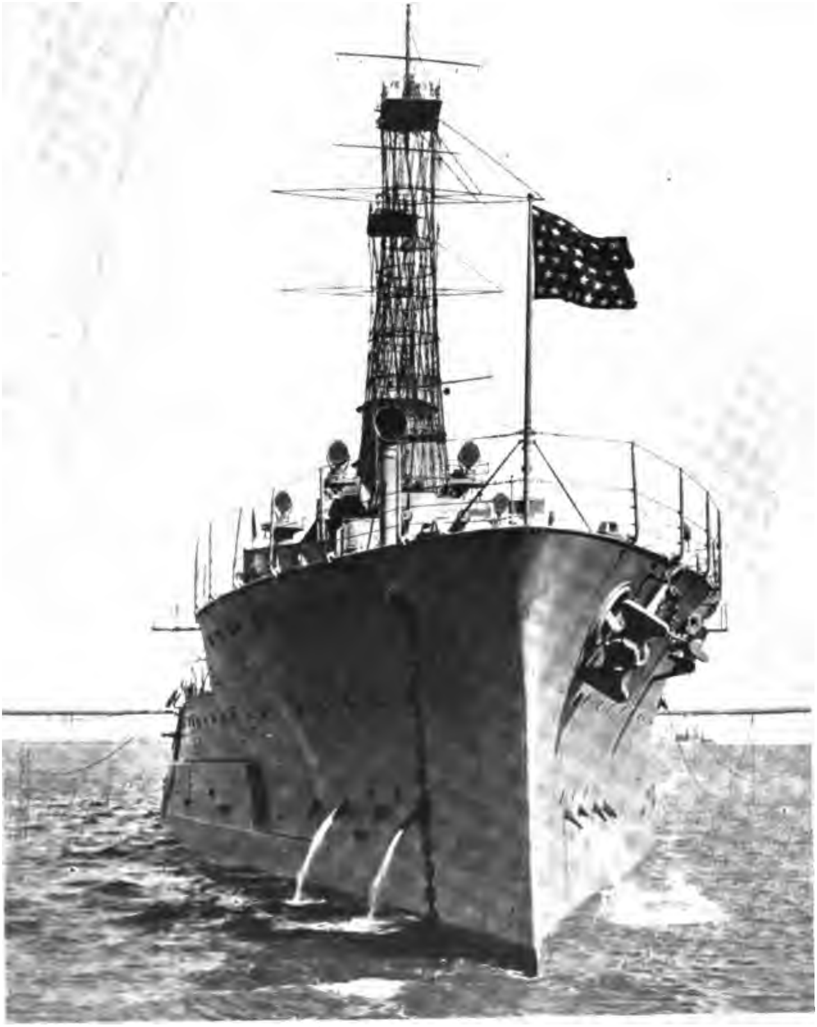


FIG. 55.

Battleship finished with regulation war color.

from the paint film only by a thin, semi-calcareous membrane which undoubtedly would allow the passage of poisonous compounds contained in the film. Without anti-fouling paints the speed of vessels would be greatly retarded by the piling up of a thick incrustation of barnacles and attached sea grass. During the building of steel ships it is the practice, as shown above, to apply a coat of red lead for protection from corrosion during the construction period. Any rust spots apparent are later on touched up and the whole under-water part immediately afterward coated with what is called an anti-corrosive marine paint. This is a light gray in color, and is made of metallic zinc, zinc oxide, alcohol, shellac, pine tar, and turpentine. Drying occurs soon after the paint is spread. A coat of red anti-fouling paint is then applied. This is composed of iron oxide, zinc oxide, mercuric oxide, alcohol, shellac, pine tar, and turpentine. By the use of such rapid-drying paints two coats may be applied to a docked vessel in a day's time and the vessel made ready for entrance into the water. This saving of time is a valuable feature, but does not embody the real reason for using quick-drying shellac paints. It has been found that for under-sea exposure they are better suited than oil paints, since the latter become soft and peel off in sheets. On the other hand, shellac paints are not durable when exposed to the air. For instance, a vessel under burden, coated with shellac bottom paint, when unloaded will present a large surface of the bottom paint to the air. Cracking and flaking of the hard film will quickly result.

Examination of a new vessel after the first three months' service will usually show that the shellac paint has given only fair service on account of the fact that it did not adhere properly to the undercoating of red-lead-linseed oil primer paint. The entirely different characteristics of the two paints has prevented amalgamation of the films. Repainting is then resorted to, with the usual ships'-bottom shellac paints, and good service is usually obtained from then on.

The writer has often doubted the efficiency of pine tar as a constituent of such paints, and suggested in place thereof, about two years ago, the water-white or amber-colored distillate from turpentine known as pine oil. This has a boiling point of over 200° C.; is miscible with alcohol-shellac solutions; has a high solvent action, and dries to a semi-resinous film possessing considerable elasticity. In tests which were conducted, paints made with the usual pigments ground with shellac dissolved in a mixture of 4 parts of alcohol and 1 part of pine oil have demonstrated their superiority over similar paints containing pine tar.

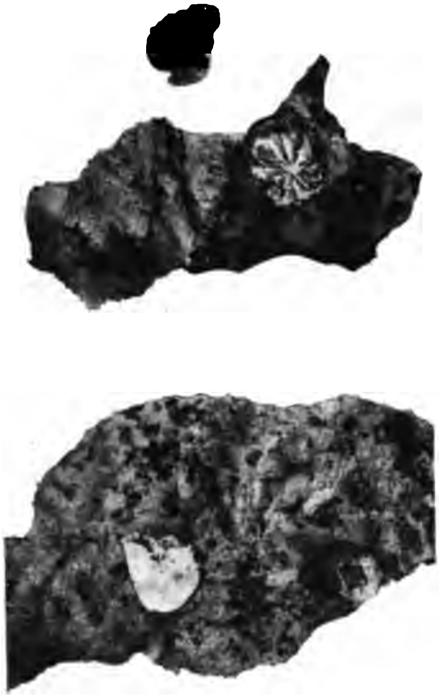


Fig. 56.

Upper view: Section of paint film removed from submerged plate test. The barnacle removed from film leaves white semi-calcareous membrane.

Lower view: Showing a barnacle attached to paint film removed from submerged test plate.

Toxic Constituents of Bottom Paints.—The efficiency of various toxic substances, such as mercury and copper, as constituents of ships'-bottom paints, have formed the basis of many practical tests that have been carried out on steel plates and in actual practice upon vessels. Mercuric chloride, when ground in a paint, has been found highly toxic to barnacles, but on account of its great solubility in water it is rapidly leached out of the film, which finally becomes inert. Mercuric oxide, on the other hand, being a solid pigment that is substantially insoluble in water, has been found a more practical material to use for the toxic ingredient of marine paints. In the presence of salt water, and especially in the presence of other pigments which possibly are electro-negative to it, the

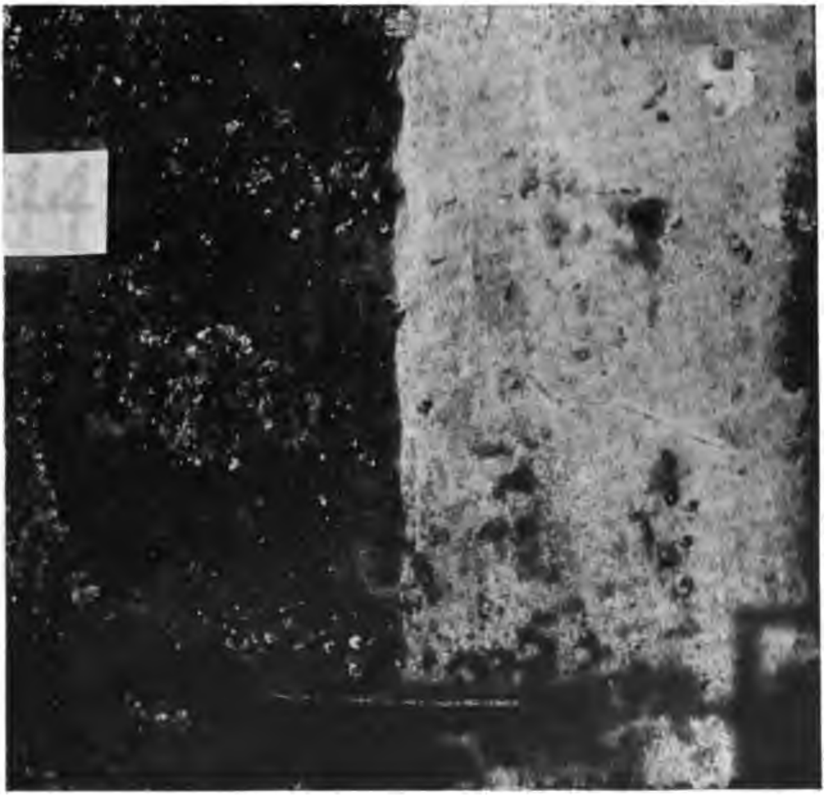
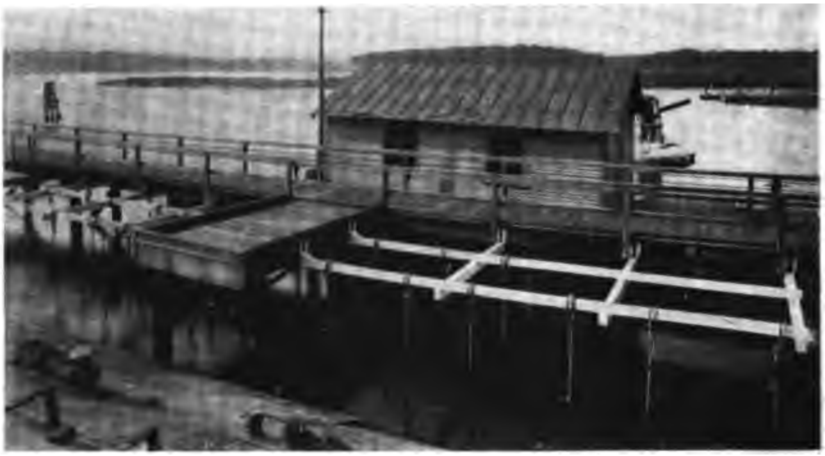


FIG. 57.

FOULING OF BOTTOM PAINTS.

View of painted steel plate after alternate exposure to salt water and air. Paint on left-hand side contains excess pine tar and is badly fouled with barnacles. Paint on right does not contain pine tar and is in excellent condition, considering time and severity of exposure.

mercuric oxide reacts and mercuric chloride in small quantities may be formed. This poisonous salt gradually becomes available as the film wears down during service, and sufficient amounts of the toxic salts are evolved to have a very poisonous effect upon attached barnacles. One objection, however, to the use of mercuric oxide has been its very high specific gravity, which causes it to subside in the containers in which the paints are stored. Unless such paints are thoroughly and carefully stirred before use, some parts of a ship upon which they might be used would be coated with films practically free of mercuric oxide, while other parts would be painted with portions in which the mercuric oxide would be in excess of the amount necessary for good results. In order to overcome this difficulty, the writer has suggested the use of various mercury soaps dissolved in turpentine or pine oil. When such soaps are added to a bottom paint, the mercury will be evenly distributed throughout the mass and the settling-out difficulty avoided.



Courtesy Navy Dept. Photo by N. E. Adamson, Jr.

FIG. 58.

Rack for suspending test plates painted with anti-fouling compositions. At ebb tide plates are exposed to air.

Copper oxides have also been used with considerable success in anti-fouling paints, the red (cuprous) oxide being especially toxic to marine animalculæ. It should be remembered, however, that red oxide of copper is electro-negative to iron, and if it should come in contact with the hull of the vessel at any point corrosion of the iron might be promoted. Copper soaps, soluble in turpentine products, might be used to advantage in connection with mercury soaps. Various salts of arsenic and lead have also been used in anti-fouling paints, but their toxicity is apparently much less than that shown by mercury and copper compounds. The writer is at present experimenting with copper cyanide, which appears to have highly toxic properties.

The function of zinc oxide or metallic zinc in bottom paints is one that has never received very much study. It is not thought that the zinc acts as a toxic substance, since it is weak in this character as compared to mercury or copper. It is apparent, however, that zinc pigments are best suited for the purpose, as practically all other types of pigments have been tried without marked success. It is well known that the value of zinc oxide in an exterior oil paint depends to some extent upon the hardness which it gives to a paint film. Since it has been found that bottom paints must produce a quick-drying, hard film, the efficiency of the pigment may depend on this characteristic. The function of the metallic zinc in the anti-corrosive paint may be of a like character, although it must be remembered that metallic zinc is electro-positive to iron, and when placed in contact with an iron surface protects the iron from corrosion, the zinc itself passing into solution.

Color Effects and Invisibility.—The present red color of bottom paints, while quite satisfactory for ships that present an almost constant water line, should be changed to a dark gray if used for colliers or other vessels that are sometimes high in the water when unloaded. Such vessels are of greater beam at many of those points where the red under-water shellac paint is applied, and a red color could easily be discerned from a hostile aëroplane at a great height, and would serve as a target during the dropping of bombs.

Attempts have been made by foreign navies during the present war to disguise the appearance of their ships by painting wave-like streaks on the bow and stern to simulate the appearance of water spray produced by fast-moving vessels, thus disguising the speed and making the vessels more deceptive targets. The problem of making a ship more invisible at a distance, through the use of certain dark-colored paints, has also been given much consideration of late. It is thought

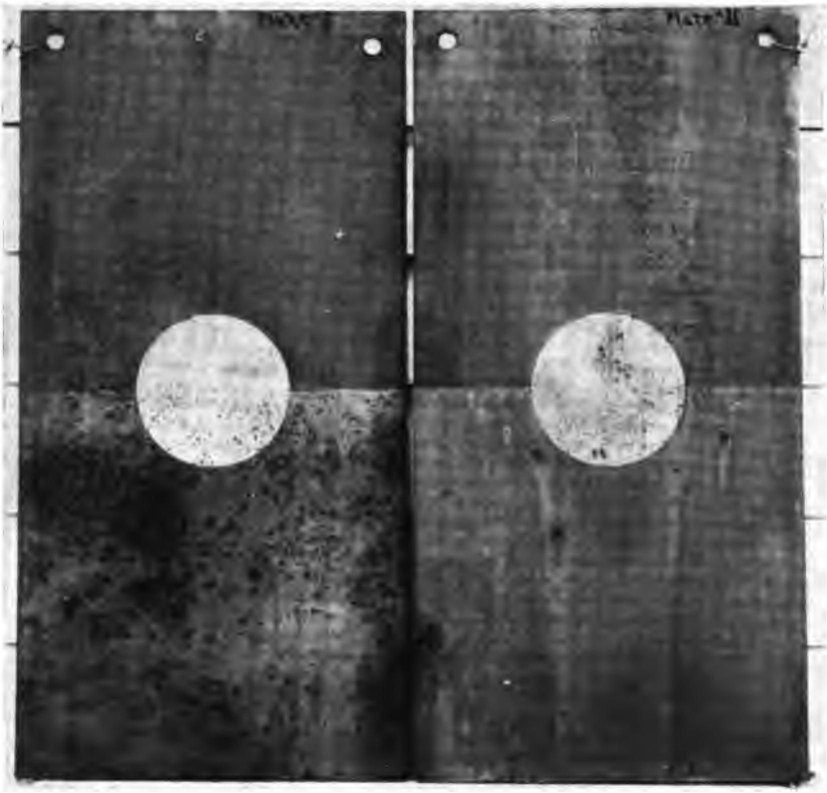


FIG. 59.

Exposed November, 1915, Washington, D. C.

TESTS ILLUSTRATING COMPARATIVE DURABILITY OF ONE AND TWO COATS OF TWO DIFFERENT TYPES OF WAR COLORS APPLIED TO STEEL PLATES.

Each plate given one coat of 94% Red Lead (a portion of which was not covered and is left bare as shown in circles). The upper half of Plates I and II were then given one and two coats respectively of Lead and Zinc Mixed Paint tinted to a Battleship Gray Color. The lower half of Plates I and II were given one and two coats respectively of Zinc and Barium Sulphate Paint tinted to a Battleship Gray Color.

that a mottled effect, produced by making a patchwork of various colors, will prove effective for this purpose. The writer believes, however, that those light-absorbing colors should be used which present the lowest light-reflecting coefficients. The results of a series of tests on the light-reflecting values of some colors are given in the chart on page 255. From a consideration of this chart, it would seem probable that various shades of gray, dark green, and blue could be used to the best advantage for this purpose, since these colors possess the greatest light-absorbing power and at the same time most closely approximate the colors shown by sea water when viewed from a distance.

It must be remembered, however, that a ship that has been made invisible when looked at from a certain angle might be visible when observed from another angle. This teaches us that in designing war colors it is very important to consider the light-diffusing properties presented by different types of films. For instance, when paints made with linseed oil, as is the usual custom, are applied to a vessel, films possessing considerable gloss are produced, and they give intense reflection of the light at certain angles, thus making the ships discernible at a distance, especially on a bright day. It should be the practice, therefore, to apply paints containing considerable volatile thinner which will effect the production of matt surface, light-diffusing films. In this connection an experiment was suggested by the writer three years ago, which might be of interest to record. The experiment was made on the battleship "Kansas" to determine whether a flat, non-reflecting war color would give satisfactory service. The painting was done early in September, the ship being given one coat of color from the truck clear down to the water's edge. The paint was slightly darker than the ordinary standard slate color. The work was started at 11 a. m., and finished early in the afternoon. At 5 p. m. the paint was dry, and presented a perfectly flat or matt surface that did not reflect the light in spots. This was considered as a distinct advantage in favor of such a paint. The composition of the color is given herewith:

Dead Flat Finish War Color.

57.50%	Sublimed Blue Lead
5.25%	Zinc Oxide
1.30%	High-grade Carbon Black
7.80%	Lithographic Linseed Oil Varnish
2.60%	Kauri Gum Japan
7.80%	Mineral Spirits
82.25%	Paste, ground fine
82.25%	Paste, as above
2.60%	Mineral Spirits
15.15%	Pure Spirits of Turpentine
100.00%	

Weight per gallon, 14½ pounds.

Pigment	64.05%
Fixed Oil	7.80%
Drier	2.60%
Volatile Matter	25.55%
	100.00%

A report made two months later on the condition of the ship showed that considerable bleaching of the color had occurred, starting at the water line and working up the sides, giving a somewhat streaked appearance. The durability was not as great as that shown by the ordinary standard war color, the salt water having visibly affected the coating. It was then recognized that a paint of this type, containing such a very low percentage of binder (linseed oil) and such a very high percentage of volatile thinner would not be suitable for exterior marine exposure for a long period of time. It was decided, however, to freshen the paint by coating it with boiled linseed oil, which was applied with waste and rubbed in on sections. This removed the effect of the salt water, and the ship, after having made passage to Genoa, Italy, and back to Cuba, showed very few discolorations, and was apparently in good condition. It has been suggested that such a paint would prove very satisfactory if reinforced with a slightly larger percentage of zinc oxide in order to prevent chalking; the addition of more black to hold the color, and the use of less turpentine or other volatile thinner.

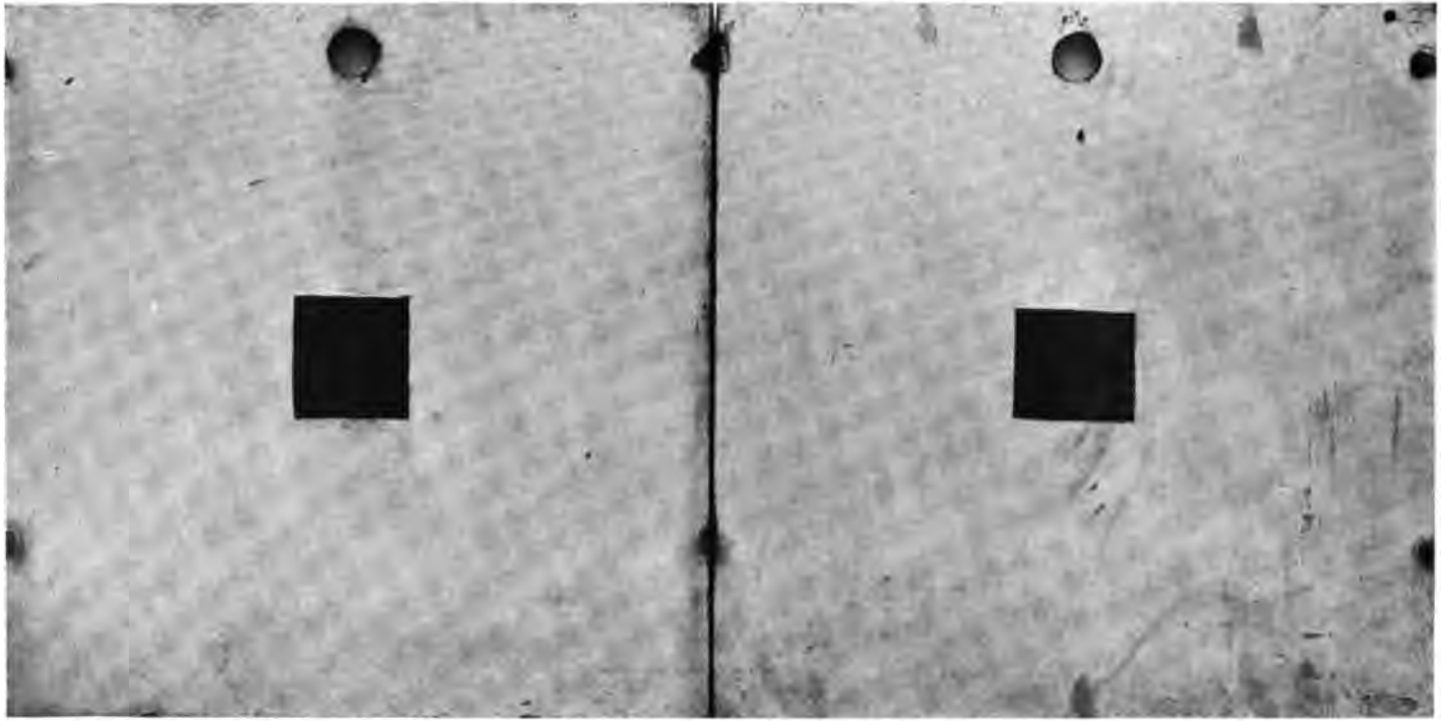


Fig. 60.

Test of Two War Colors. Exposed June, 1913.

2d and 3d coats: Blue Lead, Zinc, and Asbestine applied over a Basic Primer (see window).

2d and 3d coats: Blue Lead applied over a Basic Primer (see window at left, uncoated).

Note: Fading of color shown on each indicates that they should have been tinted with carbon black.

Water-line Paints.—At the water line of a steel vessel there is a strip that is alternately exposed to sea water and the air. Such exposure, accompanied by the abrasive action of the water, makes this strip a point of most rapid attack. Paints that will last for months on other sections of a ship are destroyed in a few weeks when applied as boot-topping (water-line) colors. The paints now used for the purpose are generally made of a mixture of iron oxide, zinc oxide, or lampblack, ground in a mixing varnish thinned with mineral spirits and drier. It is the vehicle, however, that requires most careful consideration in the design of such paints. Tung oil varnishes have been proposed on account of their water resistance, but they seem to show great peeling under the severe conditions of exposure. It is probable, however, that when mixed with certain bituminous compounds this tendency will be overcome, and a more suitable paint developed for the purpose.

Gas-resisting Whites.—In harbors where the water becomes stagnant and contaminated with sewage or waste liquor, the hydrogen sulphide gas evolved rapidly darkens white paints such as are used upon the exteriors of the cabins of vessels. Such paints are used almost exclusively for the cabin work on the coastwise merchant marine, and to a very great extent upon the hulls of vessels that ply tropical waters. The selection of a suitable paint that will be resistant to gas is an important consideration. The writer has had excellent results in tests made with a gloss white that has proved very resistant to exposure, and has been found washable and durable. This paint was prepared from basic sulphate white lead, zinc oxide, barium sulphate, silica, heavy-bodied linseed oil, refined linseed oil, turpentine, and drier.

Preservation of Tanks.—Tank painting presents one of the most difficult problems that have to be handled by those in charge of a vessel. There are many kinds of tanks, and each requires the use of specially designed paints. In coating the trimming tanks of a ship care must be observed in selecting paints which do not contain rapid evaporatives such as benzine or benzol. The fumes of such paints cause the workmen to complain of headaches, dizziness, and burning of the skin.

Fatal results are apt to follow prolonged exposure to such conditions within close spaces. The compartments are difficult of access, and cannot very well be supplied with ventilation except where air can be pumped in with portable blowers. Frequent rests in the open air and the use of paints thinned only with high boiling-point evaporatives, such as mineral spirits, are to be advocated for such work.

Ballast tanks for floating dry docks and other marine vessels need careful protection. These large tanks, which are almost completely filled with sea water when the docks are submerged, contain only about four feet of water when the docks are pumped to working level. Under these conditions, the remaining surfaces of the compartments became dry and hot when exposed to the sun. Rapid corrosion is apt to ensue unless they are properly coated inside. There is much difficulty in painting these ballast tanks, as it is hard to get them dry. due to the difficulty of providing sufficient ventilation. Electric blowers may be installed for this purpose. Probably the most satisfactory treatment involves the use of a primer of red lead and a second coat of bituminous solution, followed by a very thick coating of bituminous enamel applied hot. The enamel used for this purpose generally contains over 50% of mineral fillers, such as Portland cement.

Tanks that are used for the storage of fresh water for drinking purposes should be coated with paints that will not give a disagreeable odor or taste to the water or allow poisonous compounds to be dissolved therein. It must be remembered that all linseed-oil compounds are soluble to some slight extent in water, and in going into solution carry along traces of dissolved lead or zinc in organic combination, if lead or zinc pigments are contained in the paints. The lead compounds would be especially objectionable. A good hard drying kauri gum varnish may be used as the binder for a suitable paint, and, if desired, ordinary silica may be used for the pigment portion. This will form a perfectly transparent coating that is very water-resisting. Other water insoluble inert pigments could be used, as well as zinc oxide or lithopone, if color is desired, provided traces of zinc compounds in the water would not be considered as poisonous.

Interior Ship Paints.—The paints used on the interior of a battleship consist of lead pigments, zinc pigments, and color, ground in oils and varnishes to produce the various enamel, semi-gloss, or flat finishes that are desired. It is customary to repaint many of the interior surfaces every two or three months, in order to keep up a fresh, clean appearance. As a result, there is piled up at the end of a few years dried paint coatings of from one-half to three-quarters of an inch in thickness. The writer was present when three old battleships that had been used in the Spanish war were being scraped from stem to stern of all finishes, inside and out. Compressed air chisels were used for this purpose and the old paint chips were piled up on the decks to a depth of from six inches to a foot in many places. The writer suggested that these films be saved rather than discarded, and, as a result, there was smelted therefrom many tons of metallic lead and zinc. This represented the gradually accumulated excess burden that had been carried around by the ship for several years.

It has been found that the great heat developed in compartments or other spaces during engagements by the explosion of shells containing "T. N. T.," causes the heavily piled up interior paints to give off fumes, due to the heating of the dried oil contained in the films. While the painted surface of course remains intact and does not ignite, it has been suggested that interior paints of even greater heat-resisting character, that could be removed by washing when soiled, and replaced by new coatings, thus preventing the piling up or thickening of films, might be developed. Under such conditions it would, of course, be advisable, as at present, to keep the interior steel work primed with a suitable rust protective, which, when dry, could be coated with the fire-resisting compound. It is probable that this latter compound could be made of silicate ground with various white pigments. A rapid-drying white film would result, and it could be removed by scrubbing with water. Its heat resistance would be very great, provided it did not show cracking due to application over the metal primer. The practicability of using such a product must, however, be thoroughly determined before recommendations are made.

CHAPTER X.

ARLINGTON PAINT TESTS.

The most extensive series of panel paint tests ever conducted were those located at the Experimental Farm of the U. S. Department of Agriculture at Arlington, Va. At this place over one hundred white paints of different compositions, used upon lumber surfaces, were exposed in 1912. The tests were located in the centre of farming lands, within close proximity to a river and a railroad. The exposure was therefore typical of that to which paint is subjected in most agricultural districts. The tests were under the supervision of the leading paint experts of the United States, acting as a committee representing the American Society for Testing Materials. Inspections of the tests were annually made and reported to the Society.*

Soon after the paints were exposed rapid darkening of surface was shown by every paint which did not contain zinc oxide. In some cases the paints were discolored to such an extent that they presented a dark gray appearance. Careful examination of the surface with a magnifying glass disclosed the presence of very small particles of dried vegetation, insects and plant pollen. It was quite apparent that the surfaces of the paints had remained soft and retained the particles of dry matter carried against them by the wind. The gradual accumulation of such particles was responsible for the darkened appearance of the paints.

Over fifty of the paints used in the tests contained 25 per cent or more of zinc oxide. Every one of these zinc-containing paints remained white and clean. The zinc pigment caused the paints to dry rapidly to a firm surface, resistant to soot or particles of other matter present in the air.

Some of the tests cited above are depicted herewith. They forcibly illustrate the advisability of using zinc-containing

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* For official reports, see Proceedings of the American Society for Testing Materials, 1912-14.

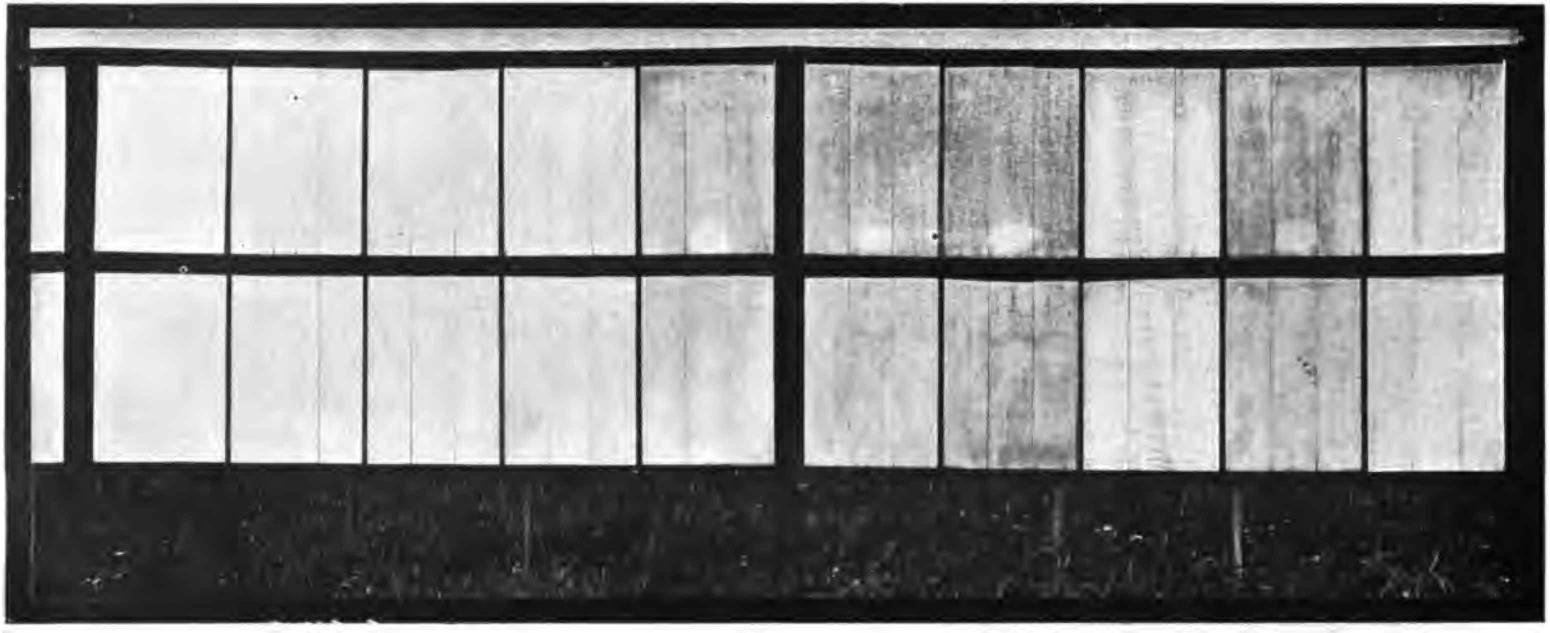

FIG. 61.

A section of the tests illustrating the value of zinc oxide in preventing the darkening of paints. The first four paints contained zinc oxide. The last six did not.

paints in the rural districts. In industrial communities, where the atmosphere is polluted with dust-laden smoke, such paints are an absolute necessity.

Prepared paints of the higher grade contain a substantial amount of zinc oxide mixed with white lead (corroded or sublimed). The inert pigments, such as silica, barytes, asbestine, whiting, china clay, etc., are used in moderate percentages in some of these products.

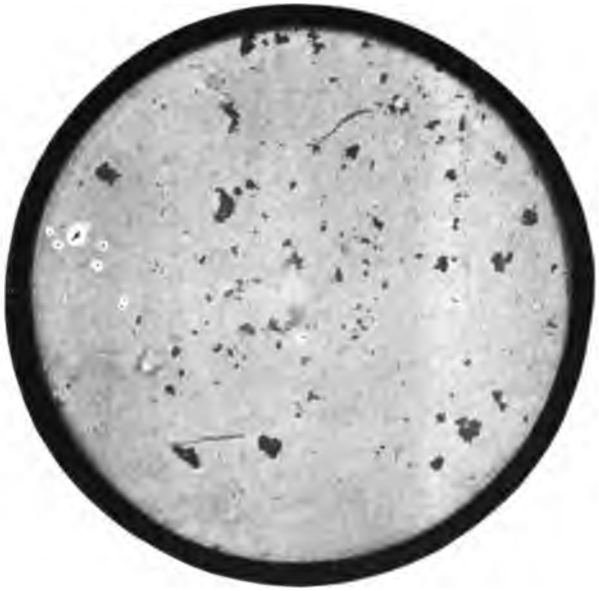

FIG. 62.

Microscopic view of lead paint which did not contain zinc oxide. Softness of paint has caused the retention of dust, plant pollen and insects, giving darkened appearance to paint.

Such paints afford the maximum wear and present the best appearance in any climate.

In the official report of the inspection committee of the American Society for Testing Materials, the following comments were made on the results of the above-described white-paint tests at Arlington.

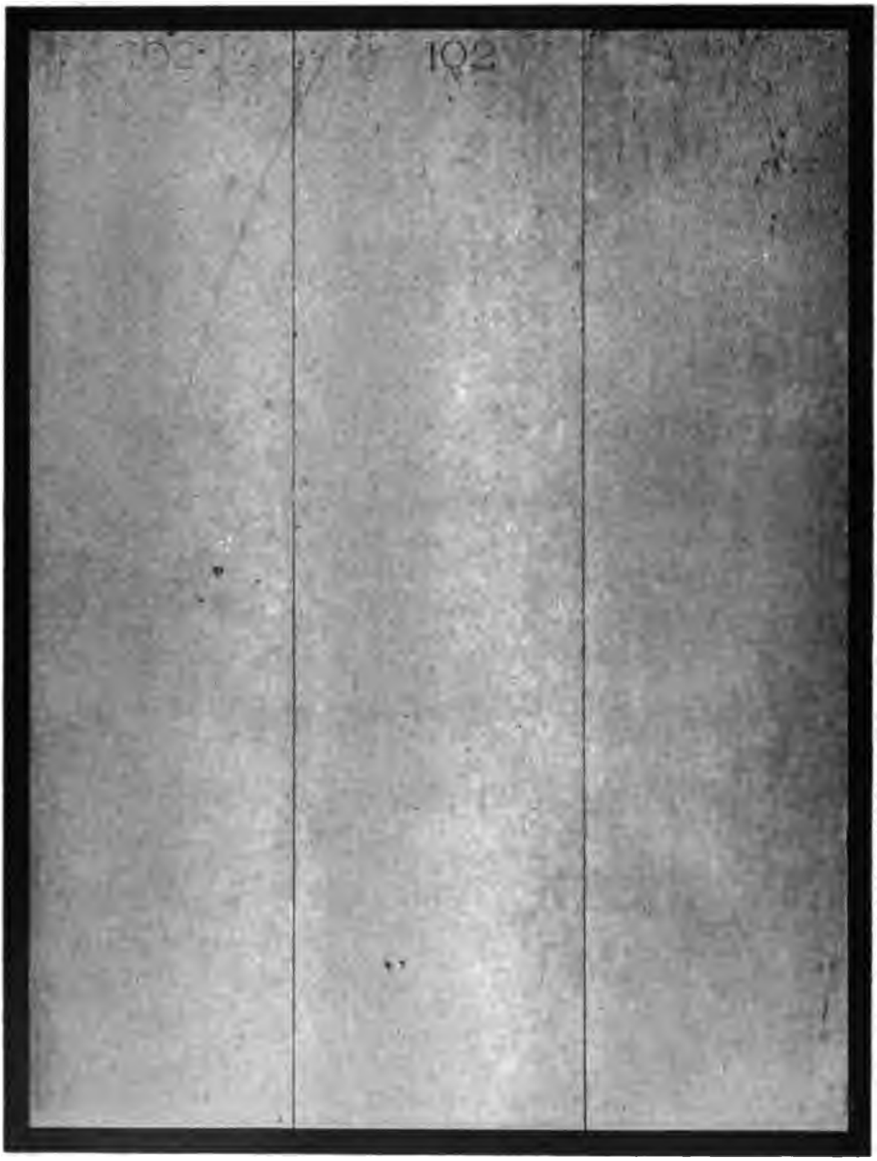

FIG. 63.

Painted with white-lead paint which did not contain zinc oxide. Darkening and checking of paint shown.

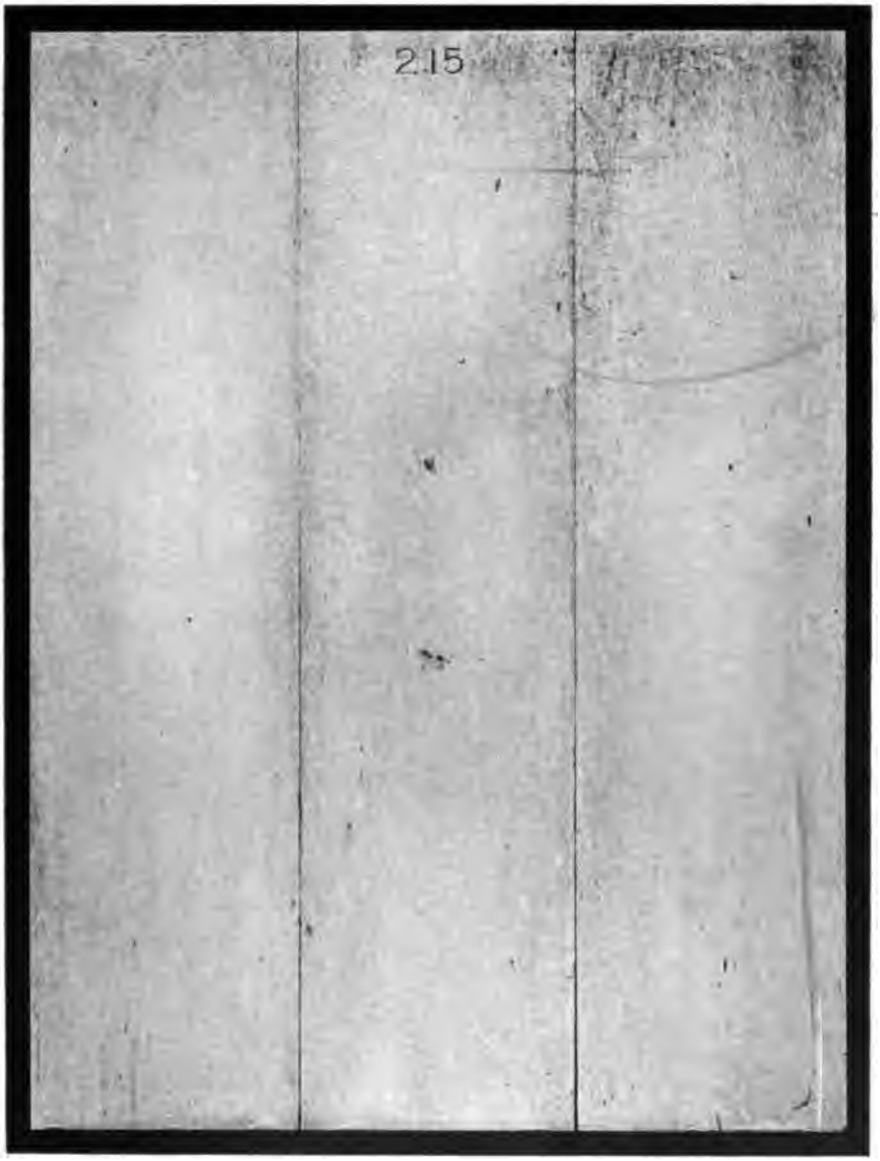

FIG. 64.

Painted with white-lead paint which did not contain zinc oxide. Darkening and checking of paint shown.

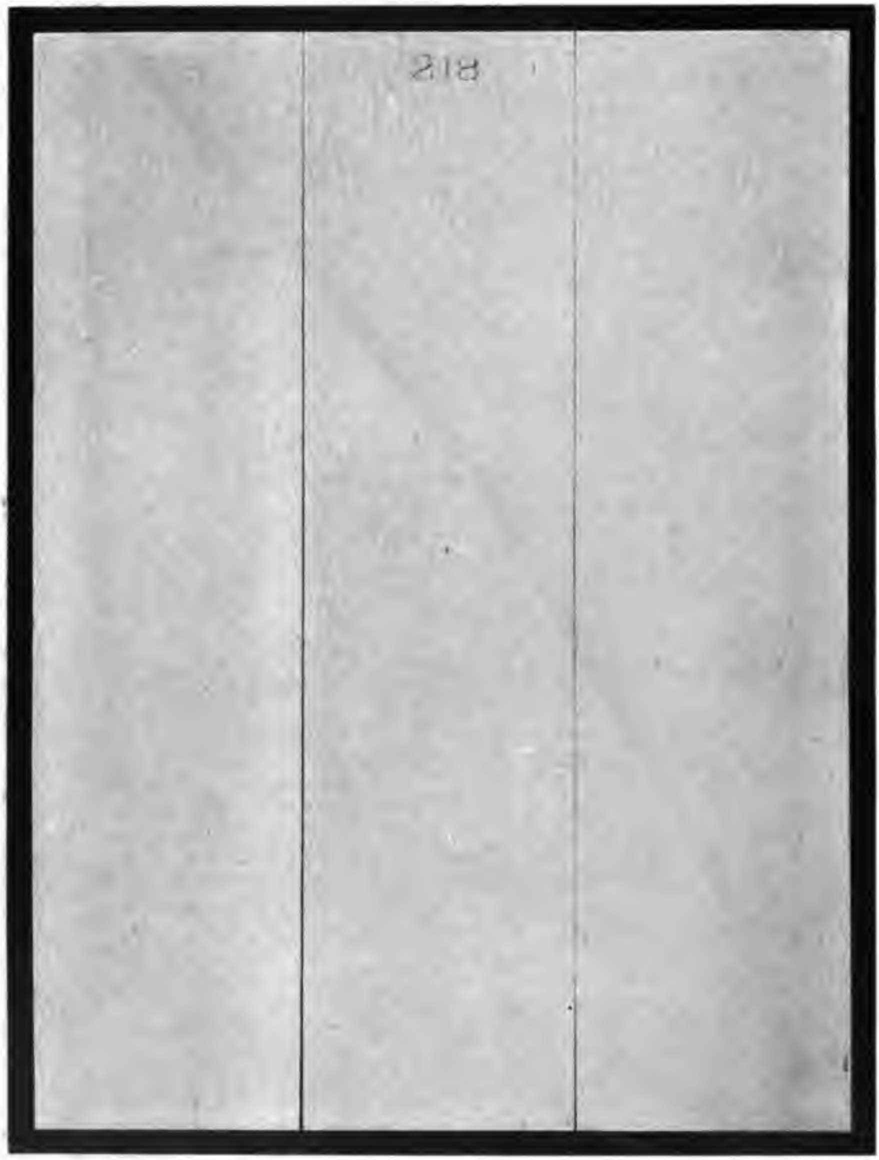

Fig. 65.
Painted with a mixture of white lead and zinc oxide. Paint is very clean and in excellent condition.

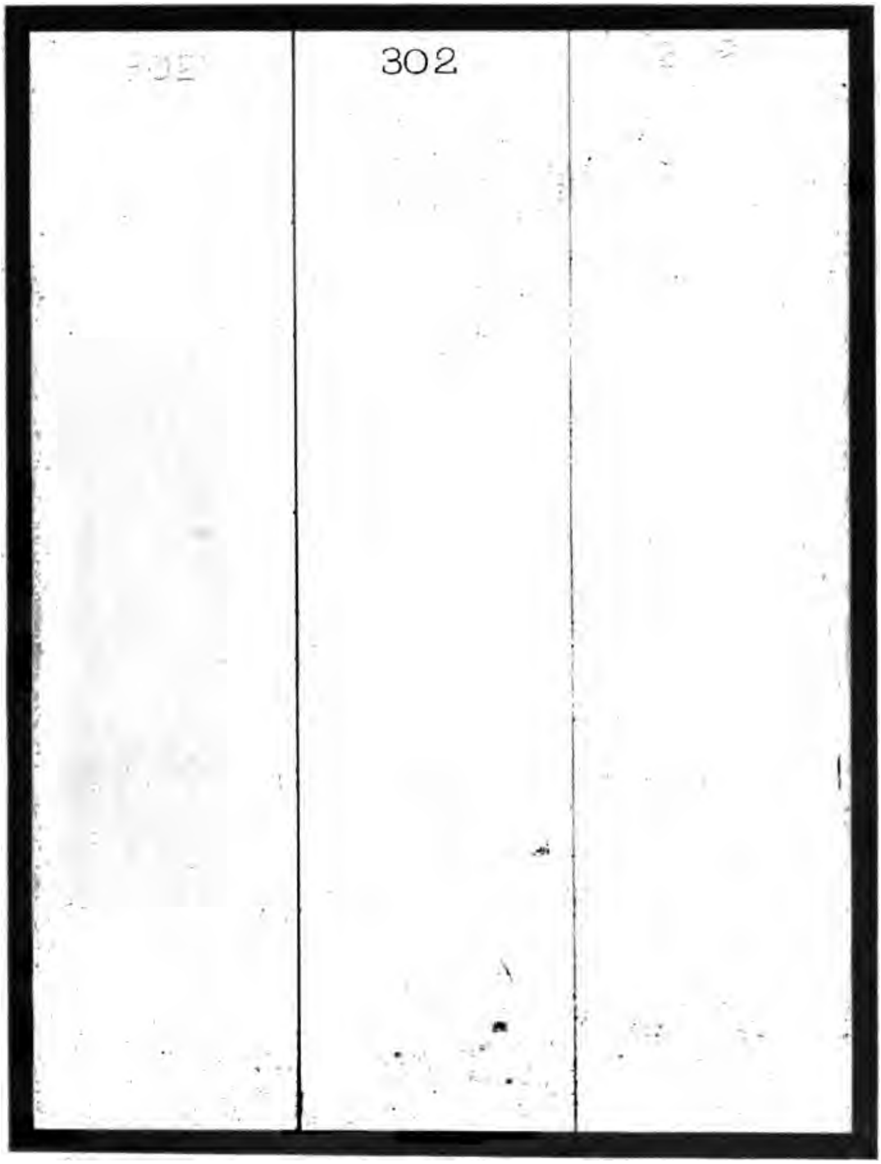

FIG. 66.

Painted with a mixture of white lead, zinc oxide and inert pigment. Paint is very clean and in excellent condition.

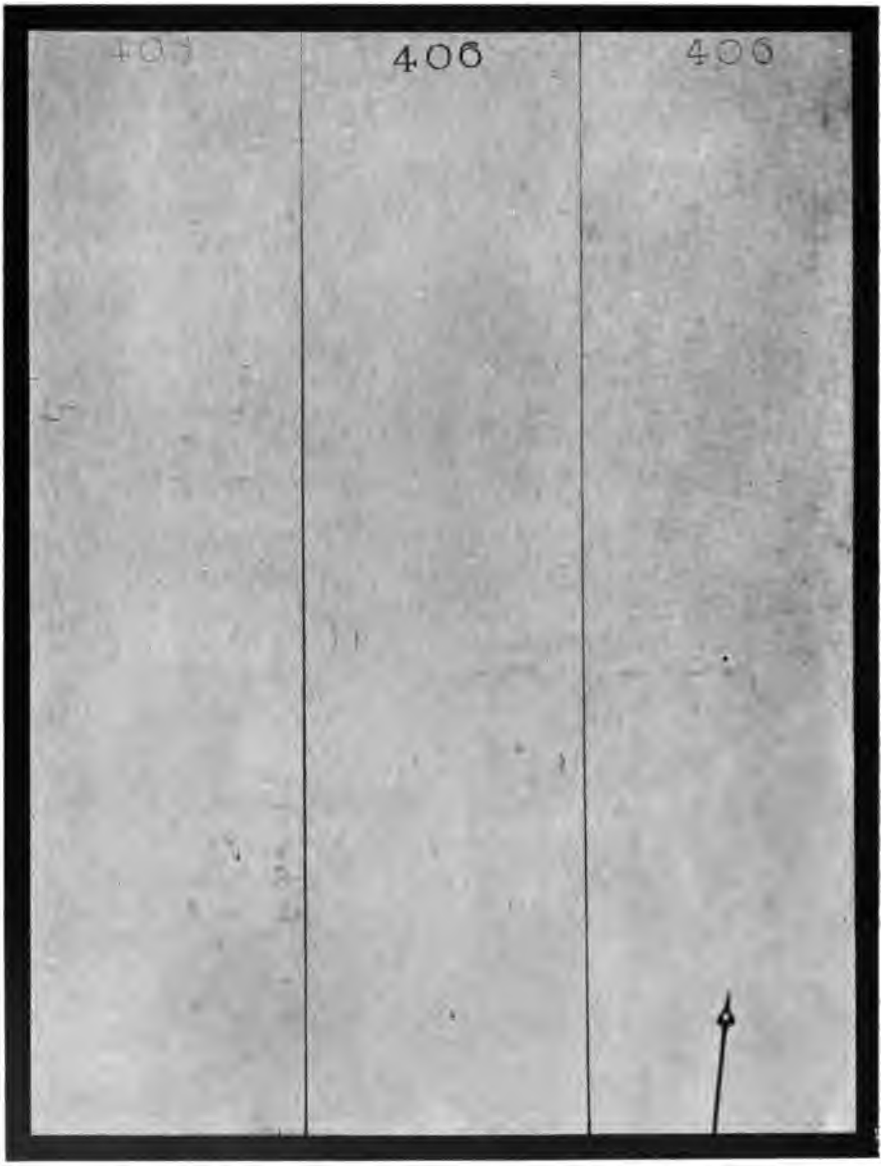

Fig. 67.

Painted with a mixture of the white leads, zinc oxide and inert pigment. **Paint is very clean and in excellent condition.**

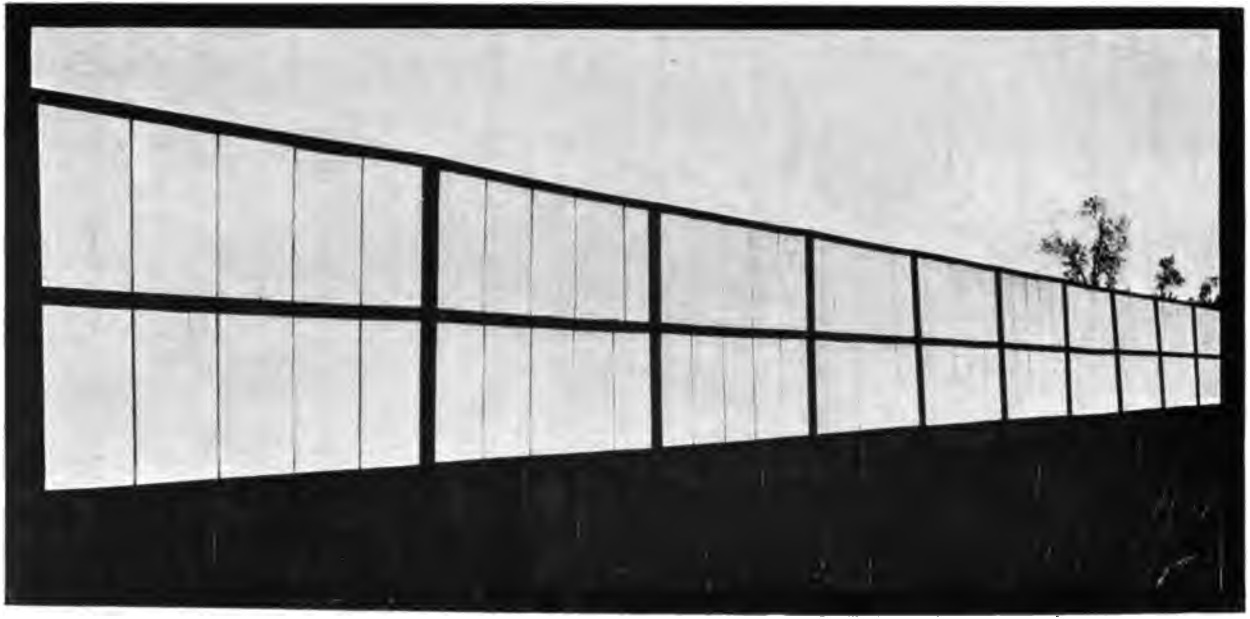

FIG. 68.

View of 48 panels, each painted with a different formula. All of these paints were made of mixtures of zinc oxide with white lead (corroded or sublimed). To some of the paints inert pigments were added. Clean white surfaces are shown by every paint.

"*Results of Inspection.*

"*Primary Pigments.*—Panels Nos. 101 to 103, inclusive, consist of the three types of basic-carbonate white lead. They show more or less checking which does not extend through all coats: they also have picked up some dirt.

"Panels Nos. 104 and 105 are zinc oxide. They show extremely fine surface checking and are very clean.

"Panel No. 106 is basic-sulphate white lead. It shows very fine surface checking and is very dirty.

"'Panel No. 107, zinc-lead white, shows no checking and surface is very clean.

"*Binary Composition.*—Panels Nos. 201 to 208, inclusive, consist of 80 per cent. of basic-carbonate white lead and 20 per cent. of one of the following pigments in the order named: zinc oxide, basic-sulphate white lead, silica, asbestine, China clay, calcium carbonate, calcium sulphate and barium sulphate. While an effort has been made to differentiate between these panels, the differences are slight except in No. 201, which is clean and white with slight checking in marked contrast to the others, which are decidedly dirty; No. 208 shows fine checking and has a medium clean surface.

"Panels Nos. 209 to 216, inclusive, consist of 50 per cent. of basic lead carbonate and 50 per cent. of one of the other pigments named in the group of Nos. 201 to 208, inclusive. Here again the mixture of basic-carbonate white lead and zinc oxide shows but fine checking and the surface is clean. Panel No. 210, composed of basic-carbonate and basic-sulphate white lead, shows no checking with a medium clean surface, while the others show a tendency to pick up dirt to a greater or less degree.

"Panels Nos. 217 to 219, inclusive, consist of 60 per cent. of basic-carbonate white lead and 40 per cent. of French Process zinc oxide, American Process zinc oxide and basic-sulphate white lead. The two panels made up with white lead and the two zinc oxides show very fine checking, but are white and clean, while the combination with basic-carbonate white lead and basic-sulphate white lead shows marked checking and is rather dirty.

"No formula is given for panel No. 220.

"Panels Nos. 221 to 227, inclusive, consist of 50 per cent. of American Process zinc oxide and 50 per cent. of one of the following pigments in the order named: basic-sulphate white lead, silica, asbestine, China clay, calcium sulphate, calcium carbonate and barium sulphate. This series is characterized by a clean, white surface and in general by an absence of checking.

"Panels Nos. 228 to 233, inclusive, consist of 50 per cent. of basic-sulphate white lead and 50 per cent. of one of the following pigments in the order named: silica, asbestine, China clay, calcium carbonate, calcium sulphate and barium sulphate. They are characterized by a dirty surface and a marked tendency to check.

"Panels Nos. 234 and 235 consist of 60 per cent. of French and American Process zinc oxide and 40 per cent. of basic-carbonate white lead. They are very clean, but show some fine checking.

"*Ternary Composition.*—Panels Nos. 301 to 307, inclusive, consist of 33 1/3 per cent. of basic-carbonate white lead, 33 1/3 per cent. of zinc oxide and 33 1/3 per cent. of one of the following pigments in the order named: basic-sulphate white lead, silica, asbestine, China clay, calcium carbonate, calicum sulphate and barium sulphate. This group is characterized by the absence of checking or fine checking and has a clean, white surface.

"Panels Nos. 308 to 314, inclusive, consist of 50 per cent. of basic-carbonate white lead, 25 per cent. of zinc oxide and 25 per cent. of one of the pigments named in the group Nos. 301 to 307, inclusive. These panels are in the same general condition as the group of Nos. 301 to 307, inclusive.

"Panels Nos. 315 to 321, inclusive, consist of 25 per cent. of basic-carbonate white lead, 50 per cent. of zinc oxide and 25 per cent. of one of the pigments named above. This group shows no checking or very fine checking with a very clean, white surface.

"Panels Nos. 322 to 328, inclusive, consist of 25 per cent. of basic-carbonate white lead, 25 per cent. zinc oxide and 50 per cent. of one of the pigments named above. Their condition is practically identical with group Nos. 315 to 321, inclusive.

"Panels Nos. 329 to 334, inclusive, consist of 33 1/3 per cent. of basic-sulphate white lead, 33 1/3 per cent. of zinc oxide and 33 1/3 per cent. of one of the following pigments in the order named: silica, asbestine, china clay, calcium carbonate, calcium sulphate and barium sulphate. This group shows no checking and a very clean, white surface, except panel No. 333, which shows a small amount of dirt.

"Panels Nos. 335 to 340, inclusive, consist of 50 per cent. of basic-sulphate white lead, 25 per cent. of zinc oxide and 25 per cent. of one of the pigments named in the group of Nos. 329 to 334, inclusive, and their condition is practically the same as that group.

"Panels Nos. 341 to 346, inclusive, consist of 25 per cent. of basic-sulphate white lead, 50 per cent. of zinc oxide and 25 per cent. of one of the pigments named in the group of Nos. 329 to 334, inclusive, and their condition is practically the same as that group.

"Panels Nos. 347 to 352, inclusive, consist of 33 1/3 per cent. of basic-carbonate white lead, 33 1/3 per cent. of basic-sulphate white lead and 33 1/3 per cent. of one of the following pigments in the order named: silica, asbestine, china clay, calcium carbonate, calcium sulphate and barium sulphate They show more or less checking with dirty surface.

"Panels Nos. 353 to 358, inclusive, consist of 50 per cent. of basic-carbonate white lead, 25 per cent. of basic-sulphate white lead and 25 per cent. of one of the pigments named in group of Nos. 347 to 352, inclusive, and their condition is about the same as that group.

"Panels Nos. 359 to 364, inclusive, consist of 25 per cent. of basic-carbonate white lead, 50 per cent. basic-sulphate white lead and 25 per cent. of one of the pigments named in group of Nos. 347 to 352, inclusive. Their condition is about the same as that group.

"'Panels Nos. 365 to 370, inclusive, consist of 25 per cent.

of basic-carbonate white lead, 25 per cent. of basic-sulphate white lead and 50 per cent. of one of the pigments named in group Nos. 347 to 352, inclusive, and their condition is practically the same as that group.

"*Quaternary Composition.*—Panels Nos. 401 to 406, inclusive, consist of 25 per cent. of basic-carbonate white lead, 25 per cent. zinc oxide, 25 per cent. of basic-sulphate white lead and 25 per cent. of one of the following pigments in the order named: silica, asbestine, china clay, calcium carbonate, calcium sulphate and barium sulphate. The condition of the group is characterized by an absence of checking or cracking and a clean, white surface.

"*Summary.*—While conclusions are not warranted from a series of incomplete exposure tests such as these, certain indications are very evident from an inspection of these panels, which have been exposed to normal atmospheric conditions for about 15 months, especially when their conditions are compared on the basis of their volume composition.

"On this basis none of the paints composed of a single primary pigment are equal to the paints made up with composite pigments except zinc-lead white, which is actually a composite pigment.

"In the binary and ternary series the groups containing zinc oxide show less cracking and checking and a whiter and cleaner surface than those groups in which it is absent.

"The present conditions also seem to warrant the statement that the quaternary series is in the best condition of any of the panels included in the test."

CHAPTER XI.

OBSERVATIONS ON PAINTED LUMBER.

Observations on the Close Relationship Between Lumber and Paint.—During the last few years the writer has visited mines from which are obtained the crude ores used for pigment manufacture, and has made inspection trips through the factories where the lead and zinc pigments, the inert pigments, and the dry colors are prepared from raw materials. From thirty to sixty thousand tons of dry pigment are annually produced by several of these factories. When to this enormous amount of pigment there is added the sixty-odd million gallons of linseed oil produced from the flax grown in the northwestern section of this country, and the thirty-odd million gallons of turpentine distilled from the oleo-resins of our native Southern pine, one can conceive of the immensity of the paint industry and the cost to the American public of keeping its property well painted. This cost represents, however, less than one per cent of the loss that would be occasioned if property should be left in an unpainted condition. The use of paint should, therefore, be considered as an economy of the first order.

The structural materials expert will admit that nearly all kinds of building materials (cement, iron, and wood), require that decoration or protection which is obtainable only through the use of paint. This is especially true of lumber, the painting of which is to be discussed below. The advocates of this material advance as one of their arguments for its continued use, the fact that frame dwellings are generally lower in cost than those made of brick or cement, and, therefore, within the reach of the average person. They also state that concrete (unpainted) is not moisture-proof and of a most unpleasing cast as contrasted with the highly decorative appearance of painted wooden houses, which will generally last for a hundred years or longer, provided a coat of paint is applied every five or six years. Such statements as to the durability of painted wood are founded upon fact, for tests have shown that moisture and fungi, the two most active agents of wood decay, are kept from the wood by the sealing action of paint. That the continued use of wood for the construction of dwellings should not, therefore, be discouraged, is the opinion held by many.

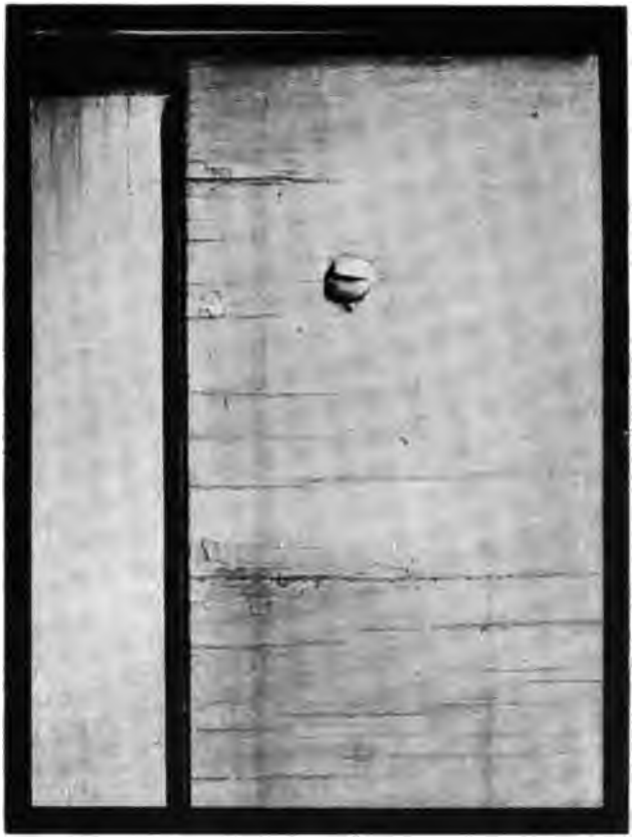

FIG. 69.

Section of painted white-pine panel exposed three years. Note expansion of boards at corner. This has affected the paint.

The weather-boarding, sheathing, sills, and other exposed portions of frame dwellings, as well as the heavy joists, studding, and uprights used for interior construction work in mills, is usually cut from the softer types of wood. These are produced by such needle-leaved trees as the pine, fir, spruce, and cypress. It is to the character of such woods that the house-painter must give his best thought. The interior wooden trim of many buildings is cut from the heavier, harder woods, grown by such broad-leaved trees as the walnut, oak, maple, and ash. The staining or varnishing of such woods constitute a problem that is not considered in this chapter.

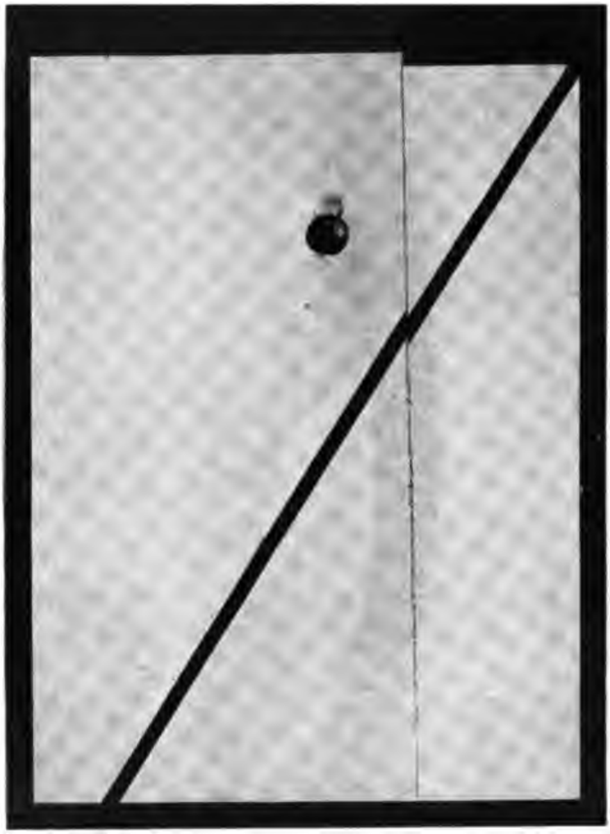

FIG. 70.

Corner of painted white-pine panel exposed three months. Expansion of boards has disturbed alignment of diagonal black stripe.

Observations on the Seasoning of Lumber and Its Contributory Effect upon the Durability of Paints.—One of the chief requisites to a successful job of painting is well-seasoned lumber. Such lumber is not only stronger, but in a much more receptive condition for paint. That paints which are deficient in elasticity are affected by the volume changes taking place in partially seasoned lumber has often been re-

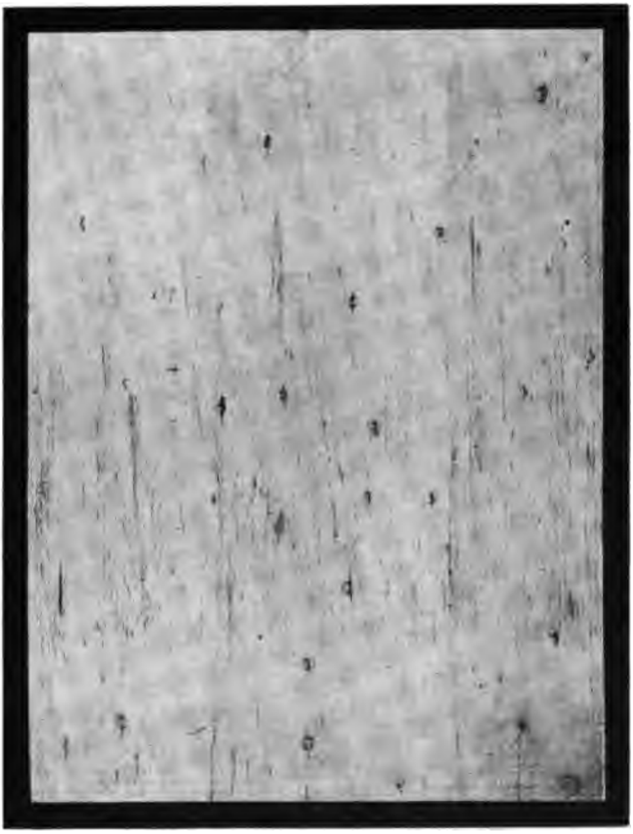

FIG. 71.

View of painted panel exposed two years. Three coats of paint had been applied without allowing sufficient time for thorough hardening or weathering. The surface shows small pits consisting of concentric rings, which resemble the effect of hail or bird shot, but are due to the brittle nature of resin that has oozed out of small resin ducts in the wood.

ferred to in the bulletins of the Scientific Section. Several examples of such changes taking place in panels which had been given three coats of paint were noticed by the writer during the summer of 1914, and have been recorded in Figures I and II. An expansion of nearly one-half inch on a three-foot white-pine panel is shown in Fig. I. In Fig. II an expansion of three-eighths inch on the same sized panel is shown in three month's time. It is apparent that among the volume changes of wood, which are responsible for the failure of inelastic paints, expansion is quite as important a factor as contraction.

It is well known that the seasoning of lumber is influenced by many factors. In warm dry climates it is rapid. In cold and damp climates it is slow. There are artificial methods of accelerating the seasoning, among which may be mentioned the old method of rafting lumber. By this process much of the sap and resin contained in the wood was removed by the action of the water, thus producing a more porous grade of wood which seasoned rapidly and afforded an excellent surface for painting. The kiln-drying of lumber may also be cited as an artificial method of seasoning and incidentally it may be well to refer to the fact that the durability of carriage and coach painting is due to the moisture-free condition of such wood, which consequently is not subject to further change in volume. When paint is applied, it is not exposed to the strains and stresses which might develop if applied to a wood containing a high percentage of water. It must be remembered, however, that kiln-dried timber is not used for structural work, and that the purpose of this paper is to treat of ordinary air-seasoned wood.

The lumber expert recognizes water in wood as existing in two forms—in the cell walls and in the pores. It is known that the free water in the pores is largely eliminated by the average period of air-seasoning without much change in the lumber. Still further seasoning eliminates some of the moisture in the cell walls, and, as a result, some slight shrinkage may take place in the wood. Lumber seasoned to this extent is, of course, in the most receptive condition for paint, as it allows deep penetration of the priming liquids which form the bonding coat. It is, however, bad practice to allow frame structures a long period of seasoning before painting. The very purpose of applying paint to timber is to prevent the accumulation of dirt and to protect the wood from the destroying fungi that assert their presence in the form of deep-seated stains. It is advisable, therefore, to apply a thin priming coat and a medium body coat of paint to all wooden structures immediately after erection. If these coats are thin, well brushed out and allowed sufficient time to dry, the wood will be coated with a film possessing valve action. Moisture from the outside will be denied ready entrance, but moisture in the wood will be allowed to escape freely during dry weather. The action of the sun will, moreover, bring to the surface, without causing bad effects, any resin or sap which might be present in the surface of the wood. From four to six months' exposure will generally be found sufficient to weather out all of the objectionable contents of the lumber. It should then re-

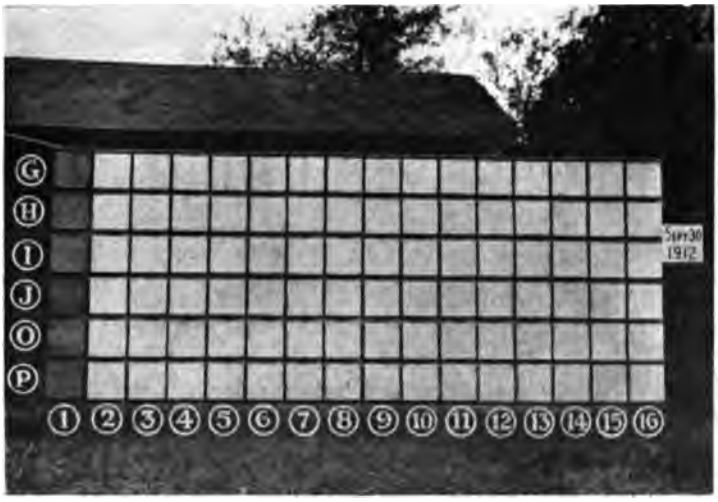

FIG. 72.

Paint test fence of cypress boards erected September 20, 1912, in St. Louis, to test the effects of various paints on cypress lumber. Each row represents one cypress board cut into sixteen panels—each panel painted with a different paint; this test made under the auspices of the Southern Cypress Manufacturers' Association.

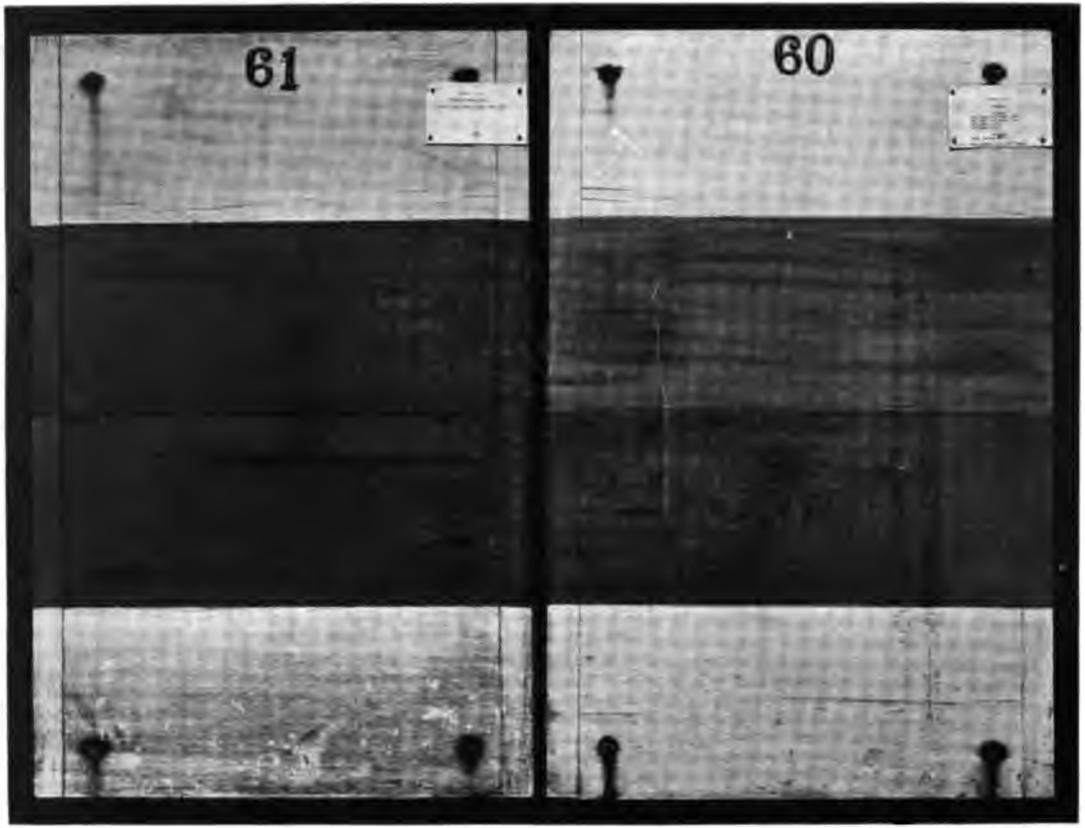

FIG. 73.

View showing condition of painted cypress panels exposed for five years. Panel 61 painted with white lead in oil. Panel 60 painted with prepared paint made on a lead and zinc base. Upper panel white, second yellow, third gray, bottom light blue. Note clean, white surface of panel 60. The tinted paints on this panel are bright and unaffected.

ceive two more coats of paint. Even the most oily or resinous types of wood may be successfully painted in this fashion, without fear of subsequent bad effects. As an instance of the durability to be obtained by such treatment, it is proper to refer to a series of white-paint tests (Fig. 72) conducted on cypress panels at St. Louis.* Some of these panels were given one coat and some two coats of paint, subsequently allowing a long period of weathering. A recent examination

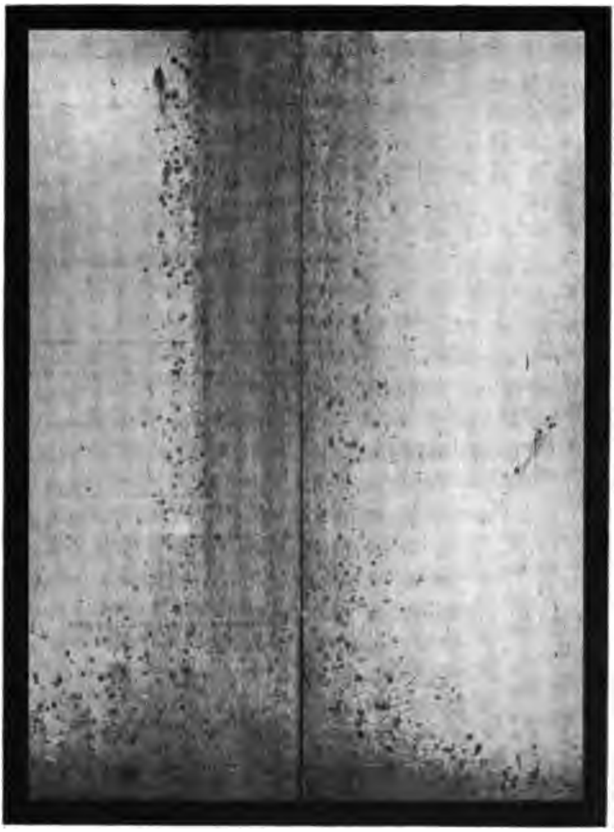

FIG. 74.

View of painted panel showing a mildewed surface. Paint applied did not dry hard, presenting a moist and tacky film.

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* See Circular 31, Educational Bureau, Paint Mfrs. Assn. of the U. S.

of the panels showed a total absence of peeling, cracking or other defects found in painting cypress and other so-called refractory woods. A perfect repainting surface was presented.

Observations on Tinted Paints Applied to Cypress.—While on the subject of cypress, it might be well to refer to a series of tests conducted at Washington, which have weathered for three years. The panels were allowed to dry for a period of ten days between coats, thus obtaining thoroughly hardened films of paint. Large percentages of thinners were used in the priming coats. Paints of the same composition for each panel, but colored to various tints, were applied. The appearance of two of the panels is shown in Fig. 73. While both single and combination pigment paints are still in good condition, it is quite apparent that the latter type is much cleaner and that the tints are brighter.

Benzol and turpentine apparently are the best diluents to use in the priming coats of paint to be applied to cypress or similar woods. This is not only shown by these tests, but also by a recent examination of the oleo-resin contained in cypress. This product, which has been termed "Cypressine," was obtained from Dr. Hermann Von Schrenk. During the kiln-drying of some cypress wood, the heat was sufficient to distill from the wood vapors which escaped at cracks in the oven and became chilled, depositing as a sticky mass upon the outside. Chemical analysis of this product indicated an acid value of 42, which is less than one-third the acid value of yellow-pine resin. Whereas ordinary resin is soluble in most of the organic solvents used as paint thinners, "Cypressine" was found soluble only in acetone, ether, benzol, grain alcohol, wood alcohol, and turpentine. Of the above solvents which could be used in a paint, benzol had the greatest effect in the cold. The fact that the alcohols are good solvents for "Cypressine" would indicate their value as the vehicle for aniline stains to be applied to cypress paneling or similar interior finish. For oil finishing, benzol would be the preferable diluent.

Observations on Mildewed Surfaces and the Inhibiting Action of Various Fungicides.—The above discussion naturally leads to a consideration of the causes and methods for the prevention of that type of fungous substance sometimes noticed upon wooden surfaces exposed in damp, warm climates and referred to by the painter as "mildew." The dried oil of a paint may under some conditions present a surface which affords a lodging place for fungi deposited by water or dust or which may be present in the oil itself, if of an infected variety. The writer has found mildew only on paints which present soft chalky films. Such paints act like fly paper in catching wind-blown matter from decayed and dried vegetation. It is such matter that contains the fungous spores which are responsible for the spotted growths referred to. The cure for this condition is to use hard-drying paints that remain smooth and clean. Prepared paints made upon a lead and zinc base are indicated for this purpose.

It has previously been proposed to add mercuric chloride (corrosive sublimate) or mercurous chloride (calomel) to single-pigment paints that are used in those localities where mildew is apt to occur. Either of these salts may be ground in a porcelain mortar in linseed oil to a smooth paste and added in small percentage to a finishing coat of paint just before use. With oil, these poisonous substances form a transparent mass like inert pigments. The writer has obtained successful results with the sulphate of mercury, which grinds in oil to a more opaque mass. Probably the most efficient fungicide is mercuric cyanide, but it is a most poisonous compound to work with. It is well to point out at this juncture that the sulphate of mercury and calomel, on account of their insoluble nature, are much less poisonous than corrosive sublimate, and, therefore, safer to have around a paint shop. It is better to have all such compounds ground in oil rather than to keep them around in dry form.

In an attempt to determine the relative toxicity of various chemicals as preventives of mildew, the writer conducted a series of small painted-panel tests. The panels were first primed with a coat of lead in oil and finished with the same paint to which had been added 2 per cent of one of the following ingredients mixed in oil: Bichloride of Mercury, Calomel, Sodium Arsenate, Barium Fluoride, Lead Acetate,

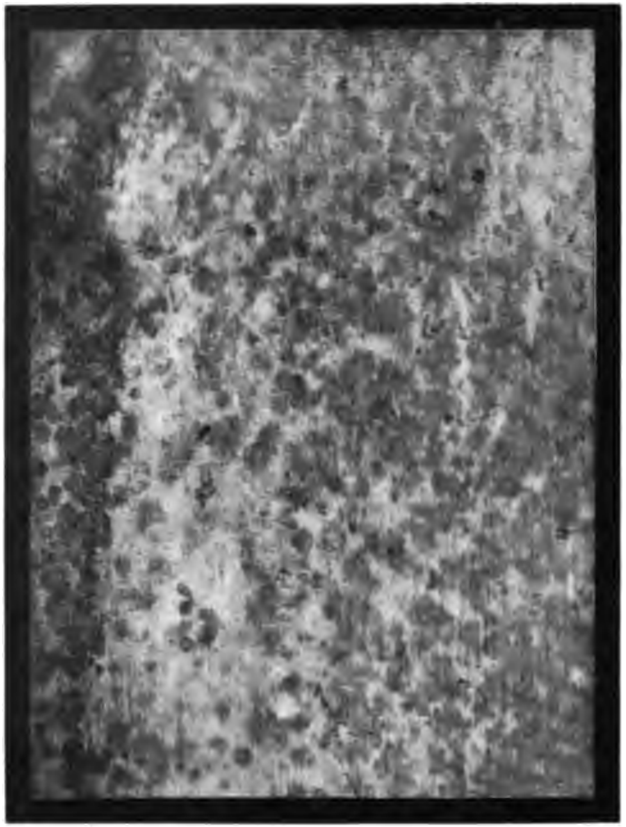

FIG. 75.

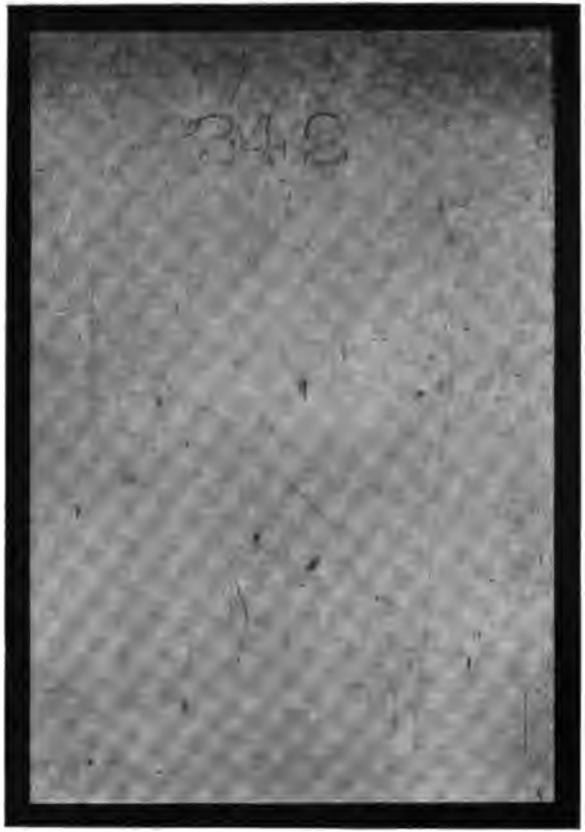

FIG. 76.

View of paints exposed to the softening action of the sun and to the effect of plant pollen from surrounding vegetation. Panel 342 contained hardening pigments to prevent softening of the film, and therefore remained white and clean.

Zinc Chloride, Mercury Soap (linoleate), Barium Soap (tungate). One panel was included, coated with paint that did not contain a fungicide. Another panel was coated with a paint made up with a sample of infected linseed oil, containing a large percentage of foots. The finished panels were dried for two weeks and then placed in a special double-walled constant-temperature cabinet (see Fig. 81). Moisture was supplied by placing water in a pan in the bottom of the cabinet. A constant temperature of 100° F. was maintained by the use of electric lights controlled by a thermostat. The temperature was recorded on a Bristol recording instrument. Diffused light was supplied through the glass in the front and back of the cabinet. Upon one end of the painted panels were sprinkled a few drops of water containing green mold that had been cultivated upon agar. Upon the other end were sprinkled a few drops of water containing a dark, wood-destroying mold. The panels were then subjected to all the conditions which tend toward the rapid production of mildew, the moisture-saturated air being constantly kept in a warm condition, only diffused light being allowed in the cabinet. A period of a month's exposure in the cabinet was insufficient to cause the development of any marked fungous growth, although some panels showed discoloration, especially those coated with the infected oil paints. These tests will be continued and reported upon later.

Observations on the Necessity of Painting Interior Mill Construction.—Throughout New England and many sections of the country, textile mills and industrial plants of different types are built with standard mill construction, using heavy timbers of yellow pine or other suitable woods for the columns, girders, etc. In dye houses and in certain finishing rooms of some of these factories, the temperature is high and the air is saturated with moisture. Such conditions are ideal for the encouragement of fungous growth, and as a result the mill timbers, if unprotected, may be rapidly attacked. Even if fungi are absent, the action of the steam-saturated air is often evidenced in a most positive manner. Such effects may be prevented by the application of suitable oil paints which protect the wood, by excluding the moisture and wood-destroying fungi.

That fungi may already be present upon the surface of unpainted wood that has been thus exposed in an unpainted condition, and that such fungi may slowly develop under a paint coating, is quite possible. In such cases it might be advisable to use, before painting, a wash which will destroy or retard the growth of the fungi. As an indication of the value of preservatives and the long life to be expected of preserved wood, it is only necessary to refer to the statement that the wooden piling used in the wharves at southern seaports would be destroyed by marine borers and similar organisms in a year's time, if left unprotected. By impregation with creosote, they will last twenty years or more. It is probable that zinc chloride would be quite as effective as creosote for this purpose, were it not for the fact that it is a water-soluble salt and would be leached out from the wood. If, however, a protective paint should be applied over the zinc-impregnated piles, they would probably last as long as the creosoted piling, provided a paint could be developed which would resist the action of the water for that period of time. In a factory, we do not have such severe conditions to contend with, and the usual high-grade oil paints may be used with most successful results. The question here involved relates, therefore, to the most efficient fungicidal wash for use upon the timber previous to the use of paint, assuming that the timber is not of the impregnated type and that some treatment is necessary. In a series of tests made by Weiss* small sections of wood were impregnated with different wood preservatives, painted white and then exposed in a fungus pit. After a period of one month bad discoloration was shown by the boards impregnated with tar or creosote oils. This would naturally be expected, for such oils have a solvent action upon linseed-oil paints and bleed through as a dark discoloration. Zinc chloride, zinc sulphate, and sodium chloride gave good results, no discoloration being shown. It is apparent from these tests that we should look toward the use of an inorganic water-soluble salt which will not adversely affect subsequently applied paints. The results of a series of tests just completed by the writer indicate that there are many chemical salts having marked fungicidal properties, which might be used for this purpose. Among the salts tested were Bicarbonate of Soda, Sodium Arsenate, Bichloride of Mercury, Lead Acetate, Barium Chloride, Zinc Chloride, Ammonium Fluoride, Copper Chloride, and Potassium Bichromate. Pure, colorless cresol crystals were also tested. Five per cent solutions of these substances were applied to separate boards which were then given three coats of paint. The boards were exposed in a damp closet heated to 100° F. for a period of three weeks. They were then placed on the roof of the laboratory, facing the sun, for an additional period of two weeks. During part of this time they were covered with ice and snow. Examination did not show peeling or any other bad effects. Although some discoloration of the priming coat was noticed when the first coat of paint was applied to the panels treated with copper and chromium salts, this discoloration was not shown in the third coat, even after exposure. Nevertheless, it would probably be safer to use one of the colorless salts which would not react with the pigment in the paint. Prominent among these could be mentioned sodium fluoride. A five per cent solution (5 pounds to 14 gallons of water) could be prepared and brushed onto the wood with a wide brush. After drying for a day or so, the paint might be applied. Inasmuch as the above-named salts act as fire retardants, their use would accomplish a double purpose, especially if used in greater concentration. For the usual grade of prepared paint, as it comes from the barrel or can, the writer would recommend the addition of three pints of turpentine or benzol to the gallon, when used for the priming coat on such work. This will result in a good foundation and give a hard bonding coat upon which to apply the finishing coats of paint.

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* Tests to Determine the Commercial Value of Wood Preservatives: Howard F. Weiss.

Observations on the Absorptive Character of Various Paint Films.—A simple experiment may be made, to show the character of a paint coating that has weathered for a considerable period of time, by driving an iron nail into the painted wood. After a month or so, the iron nail will produce considerable rust. A paint made of lead, on account of

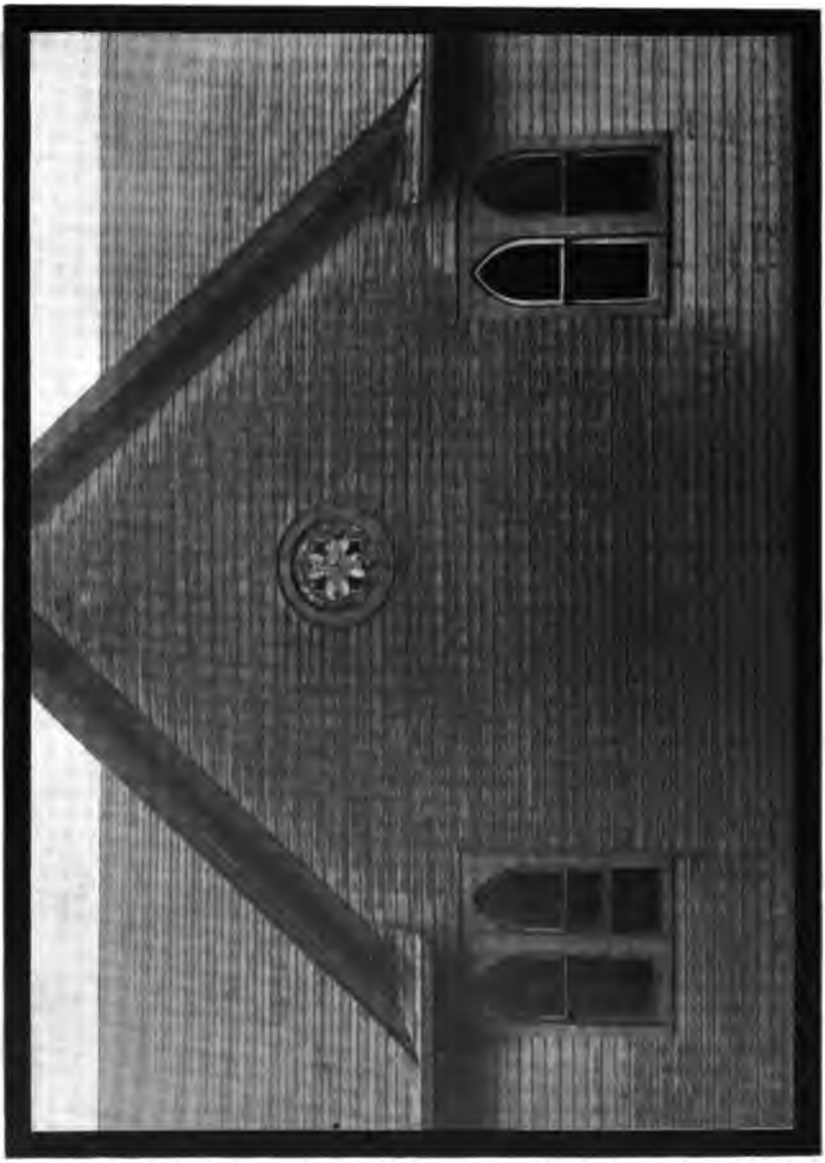

FIG. 77.

View of frame building, near Passaic River, showing darkening effects of hydrogen-sulphide gas upon white lead.

its soft and rather porous nature, will absorb the rust from the nail as it is formed. Sanding of this surface will show the rust permeated deeply through the film toward the wood. A paint made of zinc, on account of its hard and impervious surface, will not absorb the iron rust, which will run from the nail head as a light colored streak easily removed by light sanding. This same condition of film may also be shown by drawing a line upon the weathered paint surface with a fountain pen. A lead film will act like a piece of soft absorptive blotting paper, and the ink will spread out to a wide mark. A zinc film will act like a piece of highly-coated glazed paper, and the line will not spread. These tests and others are often used by the writer when examining an old painted surface. While of some minor use for that purpose, their chief virtue must be recognized in the lesson which they teach; namely, that a paint made wholly of lead is soft and porous, while one made wholly of zinc is hard and apt to be brittle. These defects are not shown by paints made of a mixture of the lead and zinc pigments, with or without a moderate percentage of the inert pigments.

Observations on Painted Surfaces Exposed to the Effect of Gases Evolved by Polluted Rivers.—During the latter part of November, 1914, the writer was invited by a friend to spend a day at Passaic, N. J., a town noted for its silk-dyeing and fabric-finishing industries, with the object of studying the wearing of paint in that community. Coming into the town, the train passed over a black-colored stream, the Passaic River, which gave forth a very unpleasant odor. I was informed that during the summer months the river pollution was greatest and at such times large quantities of hydrogen-sulphide gas were evolved. During an automobile trip along the river bank, hundreds of frame buildings were passed, nearly all of which were in a most unsightly condition. Painted surfaces which were white at one time had become dark and gloomy in appearance. That this condition was not due to the ravages of the elements was shown by the fact that comparatively new structures were as bad as the older ones. It was very evident that the hydrogen-sulphide gas from the river was responsible for the effect. The tour of examina-

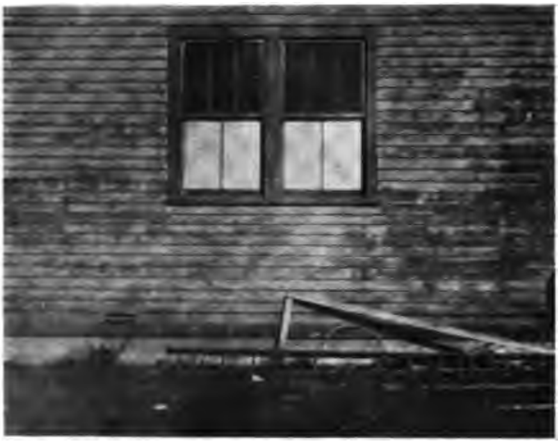

FIG. 78.

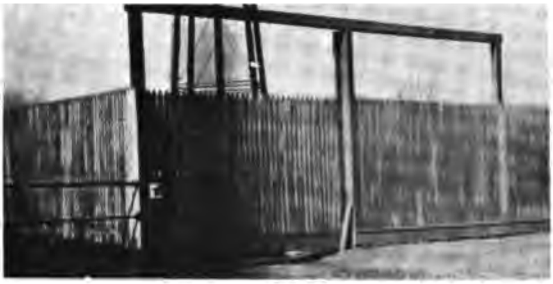

FIG. 79.

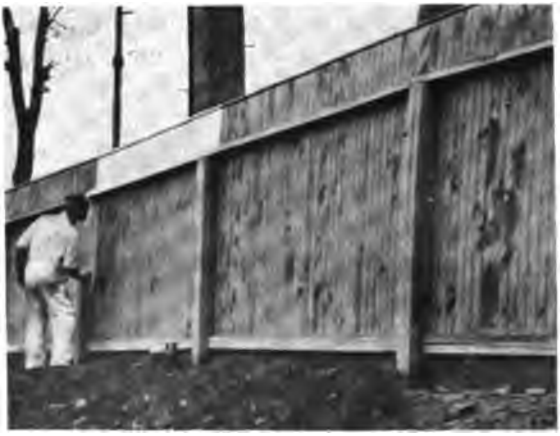

FIG. 80.

Views of wooden structures near Passaic, showing effect of hydrogen-sulphide gas from river upon white lead. These structures were from ¼ to ¾ of a mile from the river. The paint had been applied less than a year in every case.

tion led us to many parts of the city, and hundreds of darkened buildings were viewed, their aspect of decay pervading the whole community.

It was apparent that the action was most severe upon freshly-painted surfaces. Upon these could be seen large areas coated with a bluish-black deposit possessing a metallic lustre similar to that shown by a highly-polished stove or a well-blued steel rifle barrel. Between the darkened areas, sections were noticed which had not been affected to any great extent, the whole presenting a peculiar mottled appearance. An explanation of this peculiar effect was afforded by a recently primed fence which was spotted in an extravagent fashion. Close examination of the priming coat of paint showed that the darkening had not occurred to as

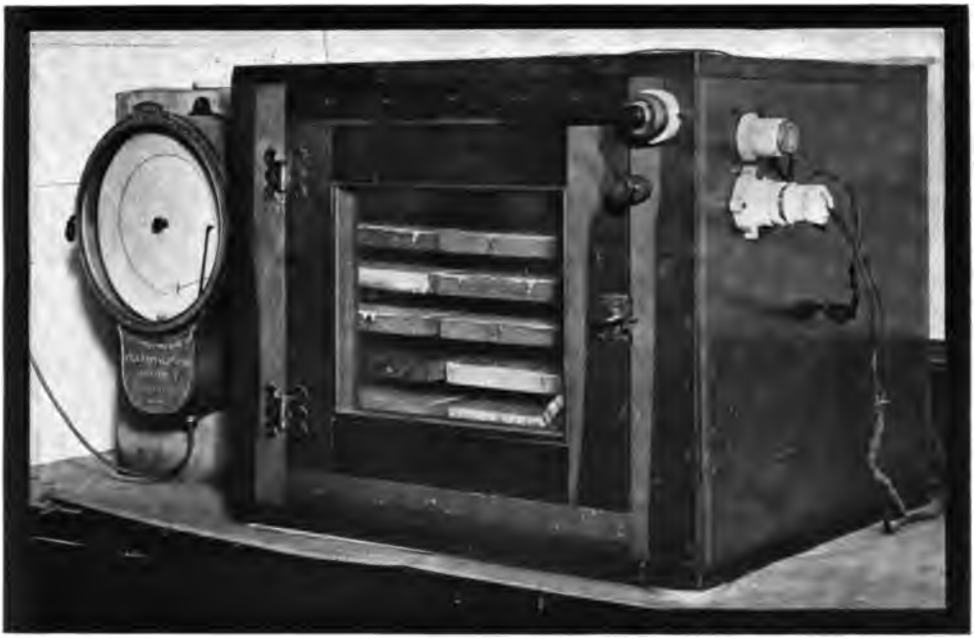

Fig. 81.

Double-walled Constant Temperature Cabinet.

View of moisture box for experiments upon the inhibition of mildew. This is also used to test the effect of gases upon painted surfaces.

great an extent upon the hard sections, where the paint was applied over knots and consequently dried with a gloss. The greatest darkening was indicated at the soft, rough sections of the wood where the oil from the paint was absorbed, leaving a coating of dry lead pigment that had but little binder.

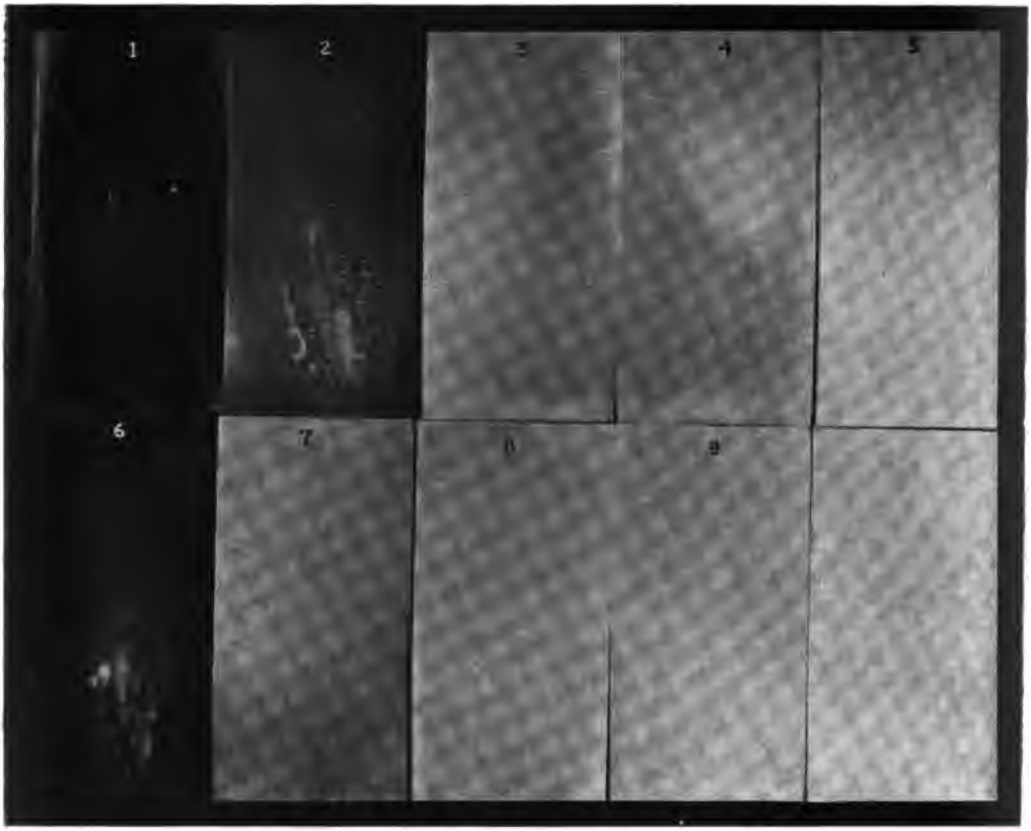

FIG. 82.

View of ten panels painted white and then placed in moisture box for three minutes during the passage of hydrogen-sulphide gas. Note various degrees of darkness shown by paints.

1. White Lead, 100%.
2. White Lead, 90%; Zinc Oxide, 10%.
3. White Lead, 50%; Zinc Oxide, 50%.
4. White Lead, 50%; Zinc Oxide, 40%; Inert Pigment, 10%.
5. Zinc Oxide, 100%.
6. White Lead, 100%.
7. White Lead, 80%; Zinc Oxide, 20% in Special Heavy-bodied Oil.
8. Lithopone, 100%.
9 and 10. Combination Pigments.

The gas, of course, attacked the drier sections of the paint with great rapidity, having more difficulty in reaching the lead pigment that was protected by a glossy coating of oil. I was informed that the black sulphide of lead upon the painted surfaces would oxidize during the winter months to the white sulphate of lead, and that this product is not attacked to such an extent upon further exposure as the original fresh coating of carbonate of lead. The oxidation, however, would probably be incomplete, and in such event would constitute another factor to account for the spotted or mottled condition shown by the houses.

During the inspection trip we came upon one house, the trim of which had been painted white. No darkening or discoloration of the paint was evident. Inquiry developed the information that a prepared paint containing zinc had been used upon the trim, but a sample of the paint was not available, and the writer could not, therefore, determine what percentage of zinc had been used. It was apparent, however, that the addition of zinc to a lead paint, produced a film that was harder and less acted upon by the gas. It is also probable that the zinc added to the gloss of the coating, and thus made it more resistant to attack. It is well known that zinc white is not affected by hydrogen sulphide, and its use should, therefore, help to solve the question of keeping paint white in industrial centers. It has been shown, however, that zinc cannot be used alone with satisfactory results. That its use in combination with lead will minimize the action of sulphide gas, is indicated by a series of tests recently made by the writer. These tests were made upon a number of white-pine panels which were coated with three coats of white paint, allowing a week between coats for drying and four weeks for hardening of the final coat. The panels were placed in a double-walled constant-temperature box, shown in Fig. 81. The temperature was maintained at about 100° F. and the air was saturated with moisture from a pan of water below the panels. A slow stream of hydrogen-sulphide gas was generated outside the box, in a Kipp generator, and passed into the box over the surface of the water. After passing through the box for two minutes the panels were removed and photographed. The results of the test are vividly shown in Fig. 82. It is apparent from these tests that 10 per cent of zinc in the final coat of paint is not sufficient to materially prevent the darkening action of the gas. It is shown, however, that larger percentages of zinc oxide have largely prevented the action of the gas upon the lead pigment. A paint of similar composition, containing 10 per cent of inert pigment, also gave very good results. Although the panels painted with these last two mentioned paints showed some slight darkening in this

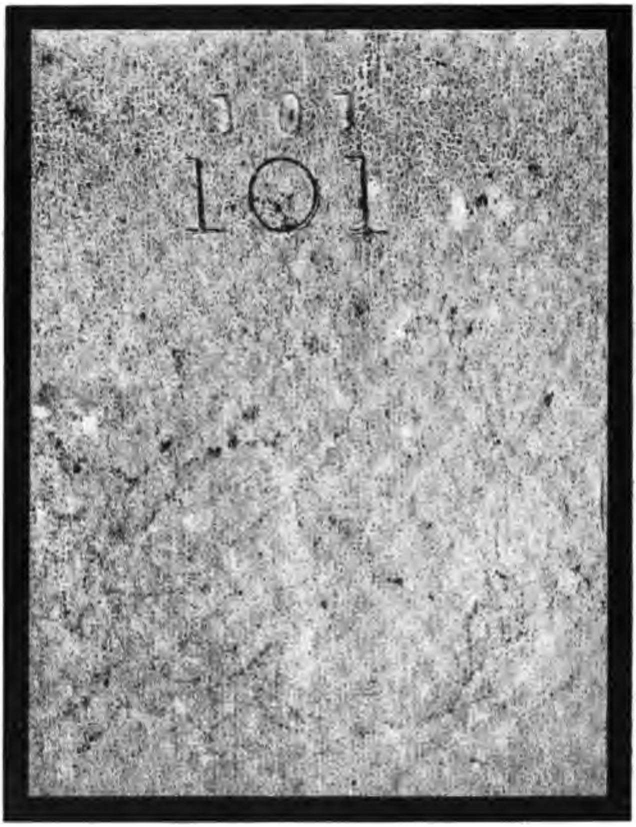

FIG. 83.

View of single-pigment paint that remained soft and weathered to a rough surface that collected dust. Type D. P.

severe test, it is probable that they would not have shown as much under actual exposure at Passaic or similar places.

Observations on Painted Lumber Exposed in Industrial Communities to the Effects of Smoke, Soot, and Gases.—The darkening of paints exposed in large industrial cities, such as Pittsburgh, has presented a problem which the writer has given considerable study. In a paper entitled "The Economic Cost of the Smoke Nuisance in Pittsburgh,"* it is stated that "*Houses in Pittsburgh, for the sake of appearances, must be*

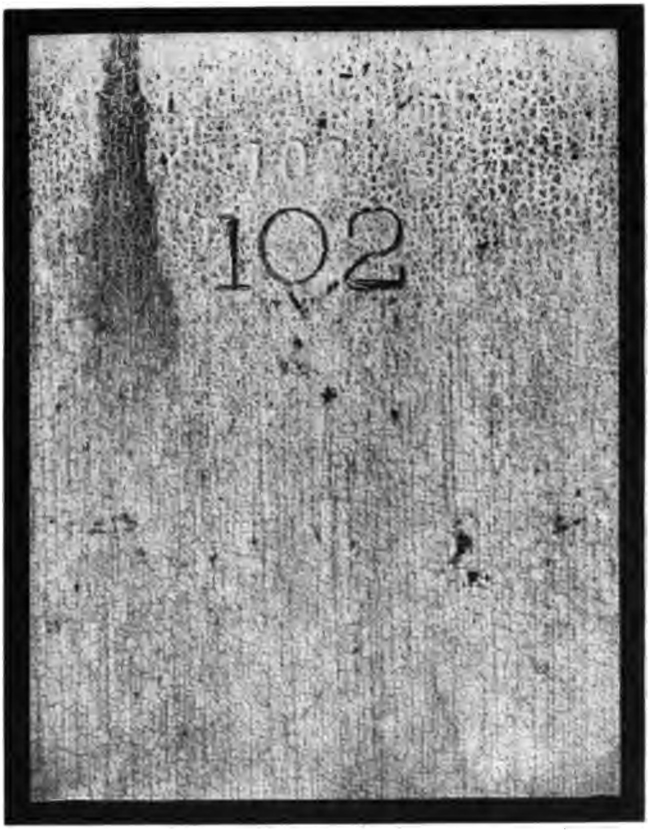

FIG. 84.

View of a corroded lead paint that remained soft and weathered to a rough surface that collected dust. Type C. P.

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* Bull. No. 4, Mellon Institute of Industrial Research.

repainted twice as often as in other cities." It is a fact, however, that frequent repainting usually arises from a desire to improve the appearance of structures and not on account of actual decay of the paint. It is also probable that stone and marble buildings must be scrubbed with acid twice as often in Pittsburgh as in other cities, if their appearance is to be considered.

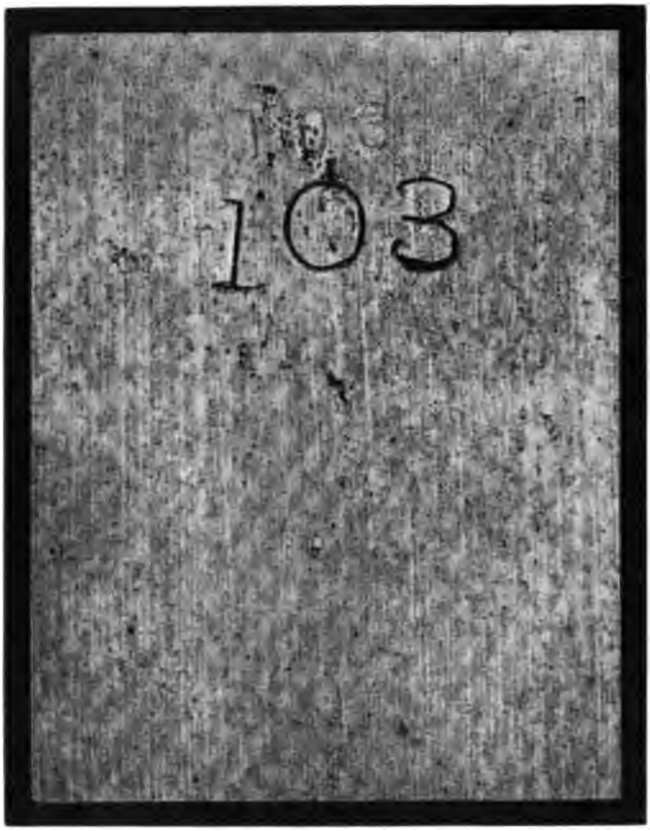

FIG. 85.

View of single-pigment paint that remained soft and weathered to a rough surface that collected dust. In better condition, however, than 101 or 102. Type M. P.

Some paints apparently last longer in Pittsburgh than in many other cities. This is partly due to the protective action of the soot. Some panels of wood painted seven years ago were recently examined by the writer. The paint was found to be in good condition and giving efficient protection to the wood. It is probable that soot protects the paint from the destructive action of the active rays of the sun. This would also indicate that such paints might afford a lodging place for fungi which grow in the absence of direct sunlight. From these considerations it would seem advisable that Pittsburghers should either repaint their homes as often as is necessary in order to keep them clean and bright, or that they should use paints which are less subject to darkening.

Among the paints exposed on the Pittsburgh test fence, a considerable difference was early shown in the resistance of the various pigments to the accumulation of soot. Those single-pigment paints which weathered to a soft, rough surface, became very dark within a short time, the rough surface offering a good holding place for deposits of soot and tar, which later on hardened to an unwashable surface. The paints which contained lead mixed with zinc or other pigments dried to harder and more glossy films. Many of these paints did not retain as much dust, or, at least, were washed fairly free of dust by the action of rains.

The writer was at one time of the belief that the darkening of paints at Pittsburgh was due to the action of hydrogen-sulphide gas. Although such gas is probably present in the Pittsburgh atmosphere to some minor extent, more recent tests have shown that the real action is caused by sulphur dioxide gas and to the accumulation of soot, carbon, and similar organic matter contained in smoke. In 1910 the writer and J. A. Schaeffer, then assistant professor of chemistry at the Carnegie Technical Schools, and Prof. K. K. Stevens of the same place made an investigation to determine the nature of the black deposit found on some of the paint tests on the fence at the rear of the athletic field. After a period of dry weather, the samples were taken. This was accomplished by light rubbing of the darkened surface of each panel with clean new sponges wetted with distilled water. The sponges were squeezed into clean glass beakers. The contents of each beaker was evaporated to a dry condition and analyzed. In our preliminary examination carbonaceous matter, iron oxide and sulphur compounds were found present. In a more recent examination Stevens* reports the following analyses of the washings from some of the panels:

Analyses of Surfaces of White Paints Exposed at Pittsburgh.

Changes Caused by the Action of Acid Gases Are Recorded and Amounts of Soot Retained by Surfaces Are Shown.

TABLE 12.

Panel No.		N-21†	W-176	W-36	W-38
Original Composition.	White Lead-Basic Carbonate..	100.00%	100.00%	75.00%	....
	White Lead-Basic Sulphate...	....	....	....	75.00%
	Zinc Oxide	....	....	25.00%	25.00%
Composition of Surface after Exposure.	Lead Sulphate	45.03%	38.00%	50.23%	84.88%
	Lead Carbonate..............	35.63%	19.60%	17.26%	....
	Zinc Oxide	3.00%	.40%	5.16%	5.00%
	Zinc Sulphate...............	....	....	....	....
	Insoluble....................	2.10%	6.66%	2.60%	2.00%
	Iron Oxide	1.40%	2.74%	3.71%	5.58%
	Carbon and Organic Matter...	12.84%	32.60%	21.04%	2.54%

These results are most interesting, and they throw considerable light upon a subject which heretofore has received but little study. It will be noted that more than 50 per cent of the lead carbonate upon the surface of the paints applied to panels N-21 and W-176 has been transformed to lead sulphate by the action of the sulphur fumes in the air of Pittsburgh. This action was, of course, preceded by the deposition upon the surface of these paints of large quantities of carbon and carbonaceous matter which adhered solidly to the rough chalked surfaces. It is well known that the rain which falls in Pittsburgh is heavily charged with the sulphur fumes picked up from the air. Such sulphur-laden water probably finds a rough, soot-coated paint to serve as an excellent blotter, and is absorbed and held upon the surface until it has sufficient

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*In a private communication to the writer.
†Three-year exposure. All others exposed two years after repainting.

opportunity to act upon the exposed pigment. In the writer's opinion, it is only the exterior surface of the paint that is thus affected, and this accounts for the great chemical changes accomplished over so short a period. It is proper to record here that the low percentage of carbon and organic matter shown on W-38 is due to the comparatively white surface of this paint as compared to W-36.

Fig. 86.

View of surface painted indoors with three coats of paint, subsequently exposing the panel outdoors to the action of the sun. The paint has softened and occluded a cobweb blown against the surface of the panel. With proper drying of each coat, a harder and more resistant surface would have been presented, and such defects prevented.

Another most interesting fact brought out by these analyses is the large percentage of iron oxide present upon the panels which were painted with white paints absolutely free from iron compounds. An average of 3 per cent of iron oxide is shown upon the surfaces of most of the white paints, while in one instance, not reported in the chart, 18 per cent of iron oxide was found present. This is not surprising, however, when we stop for a moment and think of the character of the chief industry of Pittsburgh, with its hundreds of iron and steel factories daily belching forth their products of combustion. It is, nevertheless, a most interesting fact to record that the soot and grime of Pittsburgh air does contain such a high percentage of iron. The table of analyses shows however, that the amount of iron dust is small in comparison with the amount of carbon and organic matter present. Among the constituents of the organic matter, there should be reported the presence of tar compounds, possibly due to incomplete combustion of coal. Such compounds act like mucilage and dry with the entrained free carbon and cinders to coatings which offer great resistance to washing. The writer has found that an efficient cleanser of such paints may be prepared from a neutral soap solution containing a small quantity of kerosene and some finely divided silica.

It has been stated by a contemporary that paints containing zinc oxide are acted upon by the sulphur dioxide of the air in a manner parallel to the action of such gas upon lead, and that the washing off of such paints will occur when the reaction takes place, due to the formation of water-soluble zinc sulphate. The writer, however, has not been able to fully confirm this statement or to find evidence of such action except in rare cases. The analyses of paints W-36 and W-38 which contained a considerable percentage of zinc oxide, show the absence of zinc sulphate. It is well to note here the small percentage of zinc oxide (5 per cent) found upon the surfaces of these two paints which originally contained 25 per cent of zinc oxide in the pigment portion. The non-chalking property of the zinc pigment is probably responsible for this result, the chalked lead pigments being easily removed by rubbing. In analyses made of the surface of similar paints which had

FIG. 87.

FIG. 88.

View of two lead paints, showing in one case (350) the disastrous effects of brushing the paint against the grain of the wood. (Top of panel.) The white surface of 330 is due to the use of a paint prepared upon a lead and zinc base.

weathered only two years in Washington, the writer found more zinc oxide than was originally present in the paint. This was attributed to the floating action of the light particles of zinc which would migrate to and concentrate at the surface of the paint during drying, in a manner corresponding to the floating of fine cement to the surface of trowelled concrete.

Observations on the Durability of Certain Paints Exposed to the Action of Cinders Along Railroads.—The writer has often observed with great satisfaction the excellent condition of the paints used upon small frame railroad stations throughout the country, especially those located along the suburban lines running into metropolitan centers. As a rule, such stations are painted with tinted paints, a fact which partly explains their great durability, for it has been often demonstrated that tinted paints are much more serviceable than white paints. In order to find out the composition of the paints used for railroad station maintenance, inquiry was made of the superintendents of motive power of various prominent railroads. These inquiries developed the fact that in most cases the base of the paints was made of white lead (basic carbonate or basic sulphate) and zinc oxide, ground by machinery to a paste in pure linseed oil and subsequently thinned down to the proper consistency for application. Moderate percentages of inert pigments have been used in some of these paints with good results. It is apparent that the railroads have found such combination-pigment paints to give the best results in withstanding the severe conditions to which they are subjected. It is probable that a good percentage of hard pigments is desirable in such paints and that pure oil mixed with a high-grade drier should be used for the thinner in order to form a quick-drying and fairly hard coating. Otherwise cinder darkening may occur. An example of such darkening was once brought to the writer's attention when some station sign boards were submitted, which were originally painted white. Upon exposure for a very few months, they had turned very dark. Microscopical examination of the painted surfaces showed that the paint was intact and in most excellent condition except for the presence of small particles of iron oxide and coal cinders firmly embedded in the film. Chemical analysis proved the presence of the iron oxide. The flying cinders from locomotives and the iron rust from rails and car trucks, being thrown with great force by passing trains, had become firmly attached to the paint, which evidently had been thinned with a non-drying oil or applied without drier. While such examples are not common, their study has contributed to the knowledge that will in the future serve as a guide to the painter of structures along the railroad right of way.

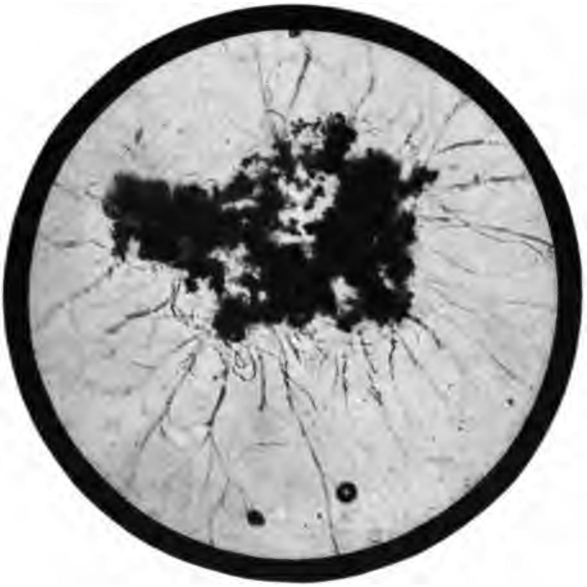

FIG. 89.

Microscopic view of fungus spores radiating from plant pollen dust particles collected on rough single-pigment paint.

Observations on the Resistance of Certain Paints, Exposed in Agricultural Districts, to the Darkening Influence of Vegetable Matter.—The writer was probably the first to attribute the darkening of some paints to the accumulation of plant pollen blown against the painted surfaces. This was pointed out in Circular No. 22,* issued in June, 1914, describing an extensive

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*The Effect of Zinc White in Paints. Circular No. 22, Scientific Section, Paint Mfrs. Asso. of the U. S.

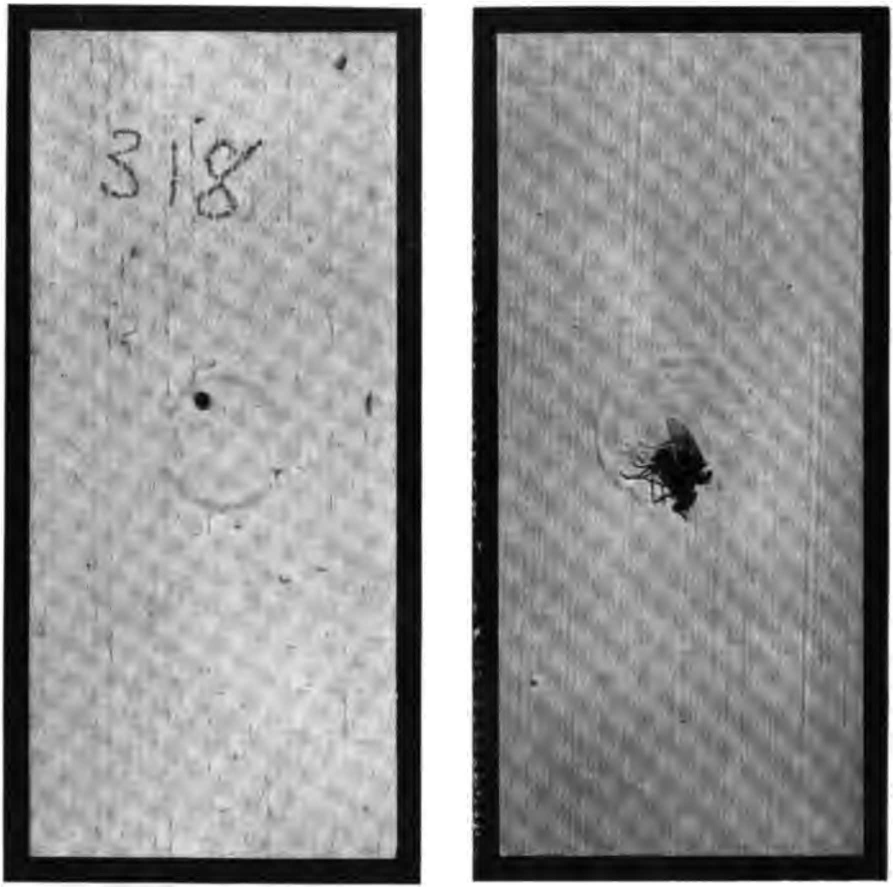

FIG. 90. FIG. 91.

EFFECT AND CAUSE.

EXPLANATION OF CURIOUS FORMATION NOTICED WHILE MAKING A DETAILED EXAMINATION OF PAINT TESTS UPON LUMBER SURFACES.

The first photograph shows a peculiar, ring-like nodule on the surface of a painted panel. This was thought at first to be due to a knot in the wood. Examination did not disclose any abnormal condition of the wood, the ring being formed of a mass of dried paint. The occurrence of the paint in this peculiar form was not explained until some tests were made several months later. At that time the writer was fortunate in securing the photograph on the right. It shows a new panel that has been freshly painted and exposed. A fly caught in the drying paint, in an endeavor to get away described a circle, the semi-dried paint becoming massed up as in the first photograph.

series of paint tests made at Arlington, Va., upon the experimental farm of the U. S. Department of Agriculture. At this place there is practically no soot or dirt in the atmosphere because of the distance from any industrial community. On some of the panels most rapid darkening was observed soon after the paints were exposed. Examination of these surfaces with a photomicrographic camera disclosed small round particles of plant pollen and dried plant material adhering to those paints which had not dried to a hard coating or which had softened under the heat of the sun. The plant pollen came from the dried plants near by. The rubbing of such paints produced a dark yellow stain which could not be removed by washing with water. The plant pollen did not stick to the lead paints which contained zinc oxide and similar film-hardening pigments. Such paints presented films which offered no lodging place for foreign matter, and thereby remained hard and clean. That the pollen-encrusted surface of paint furnishes an excellent germinating place for fungi is shown by the accompanying photomicrograph of a culture from scrapings obtained from one darkened paint, by G. Rigg and the writer. A small quantity of the scrapings was placed upon agar agar for cultivation and then photographed (April, 1914), at a magnification of 300. The transparent spores and filaments are seen radiating from the central mass of pollen.

Observations on the Proper Method of Conducting Tests of Paint upon Lumber.—The writer has been asked from time to time to outline methods of conducting paint tests upon lumber. It is, of course, possible for anyone to apply a small quantity of paint to a board and expose it to the weather, but tests of this sort should be discouraged, as they almost invariably lead to erroneous conclusions. In my opinion there is only one proper way to conduct a paint test, and that is upon a sufficiently large and practical scale to give results from which conclusions are justifiable. There are, moreover, four vital points to consider, which will have a most marked influence upon the results. These may be summed up as: *Lumber, Paint, Painter,* and *Painting,* and will be considered under such headings.

Lumber.—Unless a special test is being conducted, it is customary to select that grade and type which finds the widest use for structural purposes in the section where the tests are being made. For general work, however, it is usually advisable to select a good grade of white pine, poplar or similar wood that is fairly free of defects. Previous to cutting up into panels, the lumber should be carefully inspected, and the knotty, resinous boards rejected. To make some panels of good sections and others of bad, would obviously be unfair. Even carefully inspected lumber will vary in surface and sometimes cause defects in the paint. Tests have shown that paints may give poor results upon one section of wood, because of the sap or resin present, and give excellent results upon other sections where abnormal conditions of surface are absent. It is advisable, therefore, that each paint should be tested on more than one panel, several, if possible, and that the panels be made as large as possible, in order to afford a good brushing surface.

Paints.—The paints for a test should always be prepared on a commercial basis. Commercial practice should be observed, and batches of at least one hundred pounds (6 gallons of each formula) should be prepared in full-sized grinding and mixing machinery. The amount of oil allotted to each pigment should be normal and representative of that actually used in making paints. The work should be carried out under the supervision of a paint factory foreman whose knowledge of the grinding rates of various pigments is necessary to insure the production of properly prepared products.

Painter.—It is most important that the actual brush work should be carried out by a painter of experience. The average person, and especially the man who has some slight knowledge of the composition of paints, generally believes that he can do as good a job of painting as a painter. As a matter of fact, however, it requires years of actual service to gain the skill necessary to wield a paint brush in the proper manner. For this reason the application of test paints to panels should be made only by a competent skilled journeyman acting under the supervision of a master painter and the engineer in charge of the tests.

Painting.—The painting should follow as closely as possible the conditions of actual practice. Paints applied inside of a building, coat upon coat, and then exposed out of doors, become soft, take up dust, and early show signs of decay. For this reason, the work should be done outside whenever practicable. If the tests are being conducted during inclement weather, the painting should be done inside a well-ventilated building and twenty-four hours should be allowed for the paints to set. The panels should then be taken out of doors and placed upon a rack for a period of at least six days, so that the drying of each coat will be thoroughly hard and accomplished under outdoor exposure. This procedure should be observed for each coat.

CHAPTER XII.

IMPREGNATED PANEL TESTS.

A third series of tests conducted at Washington had for its object the investigation of the durability of paints on lumber that has been impregnated with preservative salts which may be fire retardants.

Scope of Work.—When wood is subjected to intense heat, gases of a combustible nature may be produced by the decomposition of the fibre, and in some cases through the distillation of the resins or oils present. If such gases are mixed with the vapors from certain chemicals, they become non-inflammable. Upon this principle rests the art of making fire-resistant wood, salts which are capable of volatilization at a high temperature being forced deeply into the wood by pressure. Wooden trim cut from lumber that has been treated in this fashion will, no doubt, come into general use for interior work, and in some instances for exterior work upon dwellings and other buildings. Such trim will necessarily be decorated, and information should be obtained as to the suitability of oil paints for this purpose. A series of tests to determine this question was inaugurated in and is described herewith.

Panels.—The tests were made upon a series of twenty-four white-pine panels supplied for the purpose by Mr. Howard F. Weiss, Director of the United States Forest Products Laboratory at Madison, Wis. Eighteen of the panels were impregnated in a treating-cylinder at an air pressure of 140 lbs. per sq. in., with three different types of fire-resisting salts dissolved in water. The remaining six panels were left untreated in order to use them as a basis for comparing the wearing value of the paints applied to the treated panels. All of the panels were painted with high-grade paints. One set was exposed on Young's Ocean Pier at Atlantic City, N. J.; one set at the botanical gardens in St. Louis, Mo.

Painting Data.—The panels as received from the Forest Products Laboratory were dried in the sun for a week. The edges and both faces were then primed. After drying, the screw-holes and imperfections were puttied and the surfaces sanded for the second coat. The third coat was also applied after light sanding. The penetration of the priming coat was apparently good in all cases. The panels treated with zinc chloride were darkly stained by the salt, and this discoloration showed through the priming coat of paint. The other panels were of normal color.

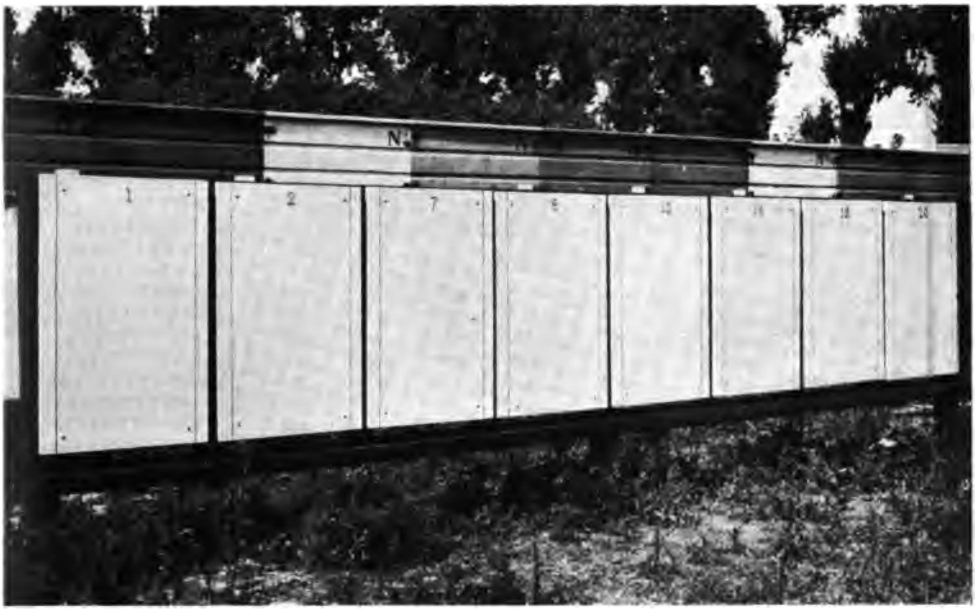

FIG. 92.

View of Impregnated Panel Tests at Washington.

All three coats of paint dried to the touch within six hours. A week was allowed between coats for drying. The panels were placed upon a framework out of doors during painting and drying, so as to be freely exposed to the action of the sun and air. The paint was applied in a practical manner by a journeyman painter under the supervision of the writer and a master painter. Data as to the composition and reduction of the paints is given below:

Composition of White Paints for Impregnated Panel Tests.

A.

Equal parts by weight of lead and zinc.

Paste ground as follows:

40% Basic Carbonate—White Lead
40% XX Zinc Oxide
20% Raw Linseed Oil

100% Paste in Oil

Made into Stout Liquid Paint as follows:

84% Paste in Oil
14% Raw Linseed Oil
2% Turpentine Drier

100%

67.2% Pigment
30.8% Oil
2.0% Drier

100.0%

Weight: 17⅛ lbs. U. S. Standard Gallon.
(This paint applied to odd-numbered panels.)

B.

30% each of Corroded White Lead, Sublimed White Lead, and Zinc Oxide, with 10% of Asbestine.

Paste ground as follows:

24% Basic Carbonate—White Lead
24% Basic Sulphate—White Lead
24% XX Zinc Oxide
8% Asbestine Pulp
20% Raw Linseed Oil

100% Paste in Oil

Made into Stout Liquid Paint as follows:

83% Paste in Oil
15% Raw Linseed Oil
2% Turpentine Drier

100%

66.4% Pigment
31.6% Oil
2.0% Drier

100.0%

Weight: 16 lbs. U. S. Standard Gallon.
(This paint applied to even-numbered panels.)

Reductions of Paints for All Panels.

1st Coat: 3 pints turpentine to 1 gallon of paint.
2d Coat: 1 pint oil and 1 pint turpentine to 1 gallon paint.
3d Coat: No reduction.

Average Spreading Rate of Paints.

1st Coat: 600 sq. ft. per gallon.
2d Coat: 620 sq. ft. per gallon.
3d Coat: 850 sq. ft. per gallon.
Date of Exposure: July, 1914.

Treatment and Arrangement of Panels.—The treatment and arrangement of the panels is shown below:

Panel No.	Treatment.	Painted with—
1	None	Formula A
2	None	" B
3	None	" A
4	None	" B
5	None	" A
6	None	" B
7	5% solution Zinc Chloride	" A
8	Ditto	" B
9	Ditto	" A
10	Ditto	" B
11	Ditto	" A
12	Ditto	" B
13	6% solution Ammonium Salts	" A
14	Ditto	" B
15	Ditto	" A
16	Ditto	" B
17	Ditto	" A
18	Ditto	" B
19	2.6% solution Sodium Fluoride	" A
20	Ditto	" B
21	Ditto	" A
22	Ditto	" B
23	Ditto	" A
24	Ditto	" B

Panels exposed at Washington:

Set No. 1	
1	2
7	8
13	14
19	20

Panels exposed at Atlantic City:

Set No. 2	
3	4
9	10
15	16
21	22

Panels exposed at St. Louis:

Set No. 3	
5	6
11	12
17	18
23	24

Preliminary Report of Forest Products Laboratory.—The preliminary report of the Forest Products Laboratory on the treatment of the wood and the tests is included herewith:

Purpose of the Work

"The purpose of the work is:

"1. To determine the possibility of successfully painting wood treated with:

- (*a*) A mixture of ammonium phosphate and ammonium sulphate.
- (*b*) Zinc chloride.
- (*c*) Sodium fluoride.

"2. By exposure to weather in different localities to determine the durability of paint on wood treated with the above salts, as compared to its durability on untreated wood of the same kind.

Materials.

Panels

"Twenty-four white-pine panels, 2 by 3 feet by 1 inch, are included in the tests. Six panels were treated with each preservative, embracing 18 panels. Six panels were untreated. For details, see working plan L-117*d*.

Preservatives

"The preservatives used were zinc chloride, 5 per cent solution; sodium fluoride, 2.6 per cent solution, and an ammonium phosphate and ammonium sulphate mixture, each chemical of 3 per cent strength, making a 6 per cent solution.

Paints

"Two paints will be used: A two-pigment paint known as paint A, and a paint with more than two pigments, known as paint B. They will be made up as follows:

Paint A =	Basic carbonate—white lead	50 parts
	Zinc oxide	50 "
	Vehicle—pure raw linseed oil, turpentine, and drier.	

Paint B =	Basic carbonate—white lead	30 parts
	Basic sulphate—white lead	30 "
	Zinc oxide	30 "
	Asbestine	10 "

Vehicle—pure raw linseed oil, turpentine, and drier.

Marking of Material

"The panels were numbered in consecutive order from 1 to 24. For details of numbers of panels and respective treatments, see the attached tables.

Method of Treatments

"In all treatments the panels were submerged in large pans filled with the preservative. These were placed in the large treating cylinder and subjected to an air pressure of 140 pounds per square inch for three hours. The absorption of the preservative was determined by weighing each panel before and after treatment. Subsequent to treatment all panels will be painted. Odd-numbered panels will be given three coats of paint A and even-numbered panels three coats of paint B.

Handling of Material Subsequent to Treatment

"The panels were dried at room temperature after treatment. It was found that the boards expanded considerably during treatment, due to the absorption of water, and it was necessary to dry them for several weeks before the panels could be assembled. This fact was more marked in the panels treated with zinc chloride.

Disposition of Material

"The finished panels were sent to the laboratory of the Institute of Industrial Research at Washington, D. C., where they were painted by a master painter under the direction of Mr. H. A. Gardner.

"The painted panels will consist of three complete sets, each set containing panels representing each treatment and paint. The panel numbers in each set will be as follows:

Set No. 1.		Set No. 2.		Set No. 3.	
1	2	3	4	5	6
7	8	9	10	11	12
13	14	15	16	17	18
19	20	21	22	23	24

"One set will be exposed to the weather at the ocean end of Young's ocean pier at Atlantic City, N. J.; one at the testing rack at the Institute of Industrial Research, Washington, D. C., and one at the laboratory of Dr. Herman von Schrenk, at St. Louis, Missouri.

"The placing of the panels and their subsequent supervision will be under the direction of the Institute of Industrial Research, representing the Paint Manufacturers' Association of the U. S. At the conclusion of the exposure tests it may be found advisable to subject the panels treated with ammonium salts to an inflammability test.

TABLE 13.

Panels Treated with Zinc Chloride

Panel No.	**Weight before treatment.**	**Weight after treatment.**	**Absorption of solution.**	**Absorption of dry salt per cubic foot.**
7	13.73	30.47	16.74	1.67
8	13.90	30.15	16.25	1.64
9	13.03	28.35	15.32	1.53
10	13.19	28.18	14.99	1.50
11	12.90	30.38	17.48	1.75
12	13.60	30 94	17.34	1.73

"NOTE.—Zinc chloride used in 5 per cent solution. Specific gravity 1.045 at beginning of treatment; at end 1.055. Temperature of solution at start 180° F.; at end of run 150° Fahrenheit. All weights taken in pounds.

TABLE 14.

Panels Treated with Ammonium Salts

Panel No.	Weight before treatment.	Weight after treatment.	Absorption of solution.	Absorption of dry salt per cubic foot.*
13	13.15	30.24	17.09	2.05
14	13.03	30.35	17.32	2.08
15	12.70	30.02	17.32	2.08
16	13.06	28.88	15.82	1.90
17	13.21	29.83	16.62	1.99
18	14.18	30.88	16.70	2.00

"NOTE.—Solution of equal parts of ammonium sulphate and ammonium phosphate used to make 6 per cent solution. Specific gravity 1.0345. Temperature at start 180° F.; at end 150° Fahrenheit. All weights taken in pounds.

TABLE 15.

Panels Treated with Sodium Fluoride

Panel No.	Weight before treatment.	Weight after treatment.	Absorption of solution.	Absorption of dry salt per cubic foot.
19	12.71	29.26	16.55	.86
20	13.36	29.33	15.97	.83
21	14.01	30.30	16.29	.86
22	13.04	29.15	16.11	.84
23	13.94	29.48	15.54	.81
24	12.88	28.68	15.80	.82

"NOTE.—Sodium fluoride solution of 2.6 per cent used. Specific gravity 1.032. Temperature at start 180° F.; at end of treatment 150° Fahrenheit. All weights taken in pounds."

Result of Tests.—After exposure for nearly eighteen months the panels gave information as to the durability of paints upon the various impregnated woods, and the results are recorded herewith.

It is apparent from these tests, photographic records of some of which are shown below, that the panels impregnated with zinc chloride or ammonium compounds do not properly hold paint, these salts exerting a destructive action upon the

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* One-half is ammonium sulphate and one-half ammonium phosphate.

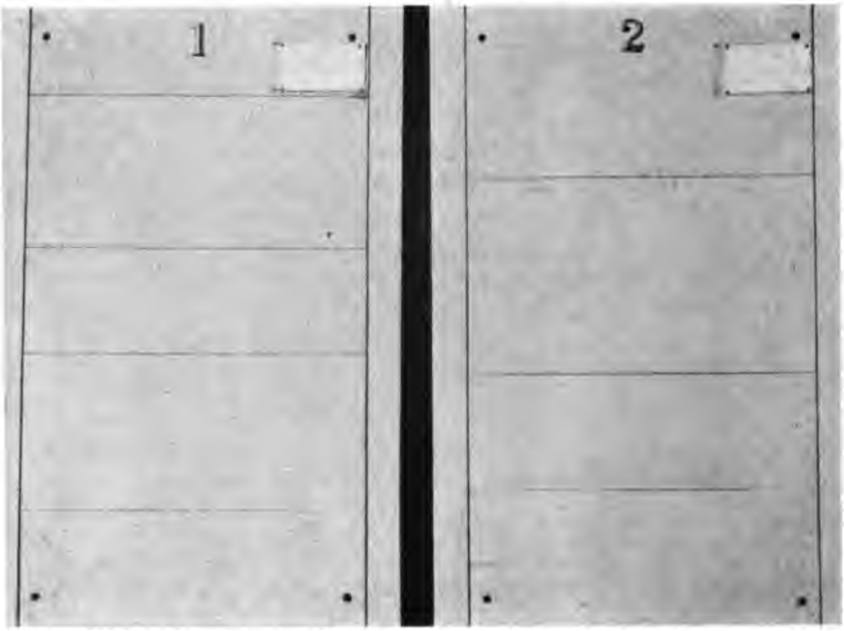

Fig. 93.
Painted Panels (Not Impregnated).
Exposure, 18 Months.

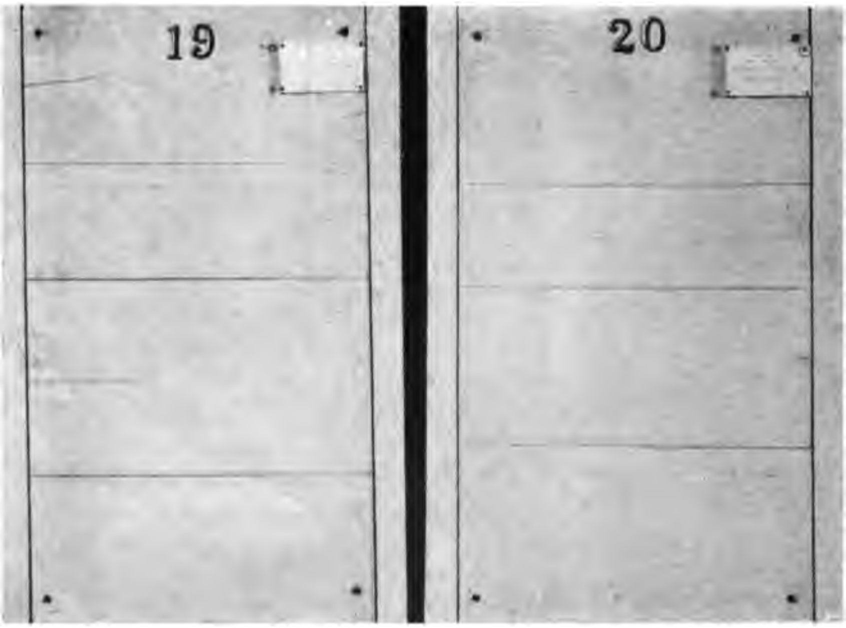

Fig. 94.
Painted Panels (Impregnated with Sodium Fluoride).
Exposure, 18 Months.

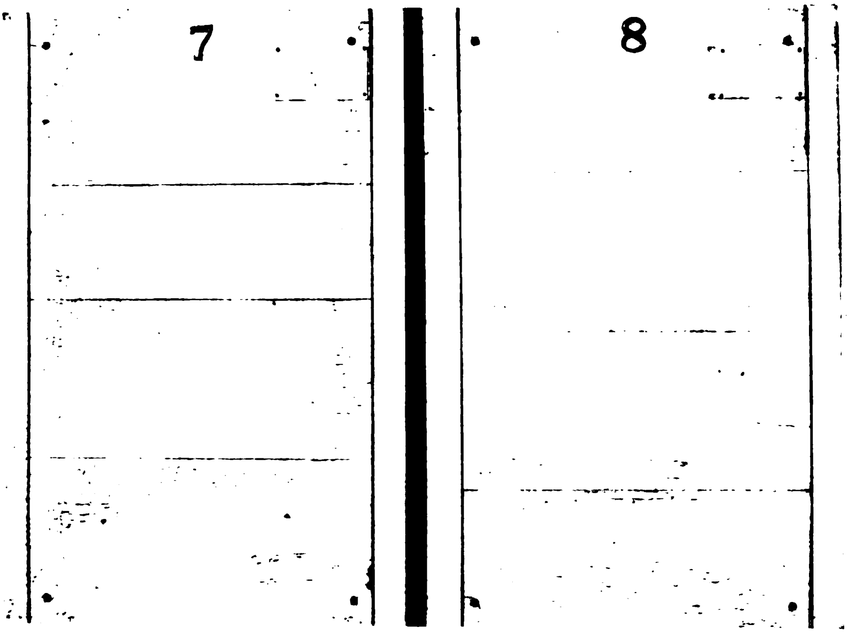

FIG. 95.
Painted Panels (Impregnated with Zinc Chloride).
Exposure, 18 Months.

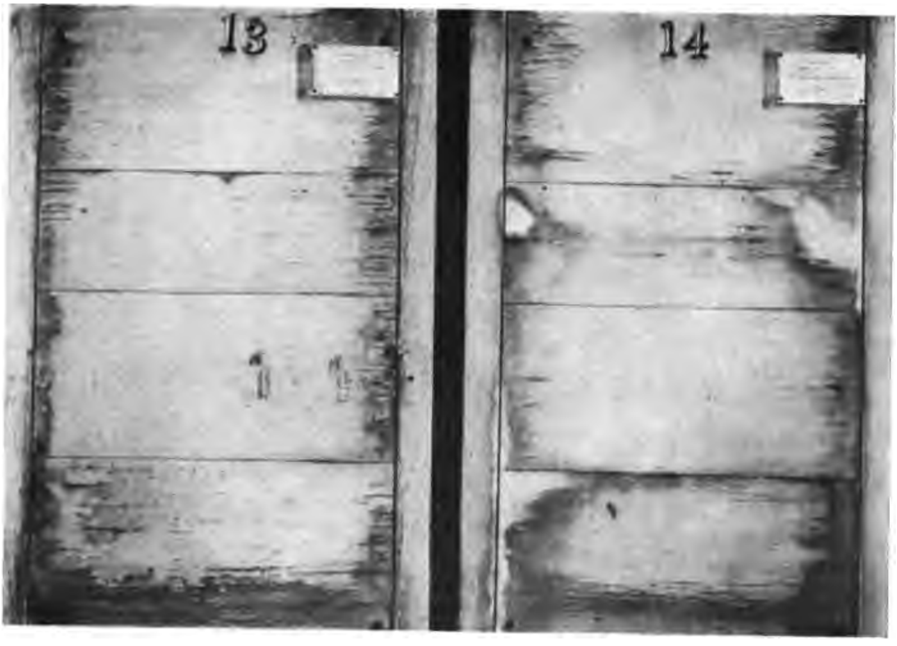

FIG. 96.
Painted Panels (Impregnated with Ammonium Salts).
Exposure, 18 Months.

oil and pigments. The ammonium salts are the worst offenders, since they produce rapid yellowing of the paint film, such discoloration having been evident soon after exposure of the painted panels. The panels treated with sodium fluoride, however, were in an excellent state of preservation, there being no visible difference between these and the painted panels which were not impregnated. The high toxic value of sodium fluoride, as well as the fire-resisting properties, make it well adapted for impregnation purposes, and it is probable that there will be a considerable use for wooden trim that has been impregnated with this salt. When such wood is used for exterior or interior work on buildings, the wood may safely be decorated with high-grade prepared linseed oil paints.

CHAPTER XIII.

FIRE-RETARDANT PAINTS FOR SHINGLES AND OTHER WOODEN STRUCTURES.

As the result of legislation prohibiting the use of wooden shingles in certain sections of the country and restrictions placed upon other forms of wooden construction, owing to the alleged danger of fire, the writer has made an extensive investigation of paints to retard ignition of wood upon which they are used, especially shingle roofs.

It would appear to the writer that this popular form of roofing material will always be used to a considerable extent. Its moderate cost, light weight, low heat conductivity,* wide application, and durability, are properties which recommend its use upon dwellings, barns, and other structures of this type. There is recorded evidence to show that the better grades of shingles have weathered in some instances for over a hundred years upon the roofs of dwellings, and have afforded during such time a high degree of resistance to the elements. In this connection, it is of interest to cite the durability of the shingled roof of General Washington's colonial mansion overlooking the Potomac at Mount Vernon, Va.† Originally covered with cypress shingles in 1743, the roof has since been patched but twice, at periods about sixty years apart. During the latter part of 1913 the roof was again mended. Although producers of some other types of roofing materials may claim that their products would have proved quite as durable, it is probable that they have no similar century-long service records to substantiate such claims. Moreover, it is likely that such manufacturers, when discussing the advantages of different kinds of roofing, emphasize the fire-refractory nature of their own products, but refer to the wooden shingle as constituting the greatest fire menace of the day.

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* The writer conducted a series of laboratory tests to determine the heat-deflecting properties of various types of roofing materials. Miniature houses were roofed with bare shingles, painted shingles, tin, and stone. Thermometers were inserted in the end of each house. The houses were placed in an oven heated to 150° C. At the end of 15 minutes, thermometric readings were taken. The interior of the houses roofed with stone and tin showed a much higher temperature than those roofed with shingles. The house with the roof covered with painted shingles showed the lowest temperature. On account of the heat-deflecting properties of shingles they will probably always find a wide application in warm climates. Shingled dwellings are much cooler in the summer than metal-clad or stone-roofed dwellings.

† *Lumber World Review*, December 25, 1913.

Let us attempt right here to point out all of the most serious charges that could be made against the wooden shingle. It is a well-recognized fact that with the growth of communities, and the consequent rise in land values, it has been found necessary to build structures in close proximity. Coupled with this condition, we have the ever-present railroad, with its frequently passing locomotives, constantly pouring forth volumes of smoke studded with glowing coals. These hot cinders may readily find their way in a high wind to the roofs of shingled structures. The sparks from dwelling and factory chimneys are, moreover, a constant source of danger to the shingled roof. The fuzzy surface of many types of new shingles, the tinder-dry condition of old shingles, and the warped edges of weather-beaten and sun-curled shingles are all factors which make shingled roofs readily inflammable. Although the writer has pointed out in the foregoing discussion the many disadvantages of the wooden shingle, the situation is not as serious as it might at first appear. Very few structural materials have ever been made which have proved satisfactory for roofing or other building purposes without some surface treatment. If iron or steel sheets are exposed to the weather they will rapidly corrode and rust away to a mere lace-like skeleton of their original form. The application of suitable paint coatings at proper intervals, however, will preserve such metal sheets for an indefinite period of time. Nearly all forms of cement or stone work will check, crack, absorb large quantities of moisture, and become unpleasing in appearance, unless properly treated with protective paints. The weather-boarding and wooden trim of all kinds of structures would soon rot and decay if left in an unpainted condition. It is evident that "paint is the preserver of all things structural," and that we must look to the use of paint for the solution of the problems under consideration.

The selection of a proper shingle paint is a matter of considerable importance. In the first place, shingle paints should not be confused with "shingle stains." The latter, as a rule, consist of creosote oils colored with a small amount of mineral or chemical color pigment ground in linseed oil. When shingles are treated with such stains, either by brushing or dipping, they present a very pleasing appearance, and become to a great extent preserved from ordinary forms of decay. Stained shingles, however, do not offer any marked resistance to combustion when in contact with fire. On this account, the use of stained shingles upon roofs will probably be discontinued to some extent with the advent of a demand for shingled roofs treated with fire-retarding paints.

Fire-retarding paints may properly be divided into two groups, one of which is represented by prepared paints made of linseed oil and mineral pigments and the other by paints which do not contain linseed oil.

The term "prepared paint" refers to that type of paint which is so widely used throughout the rural districts to decorate and preserve dwellings, barns, and similar outbuildings. In the manufacture of these prepared paints various metallic and mineral pigments (white leads, oxides of zinc, etc.), in a finely divided and carefully prepared form, are ground in linseed oil and mixed with a moderate amount of drier and thinner. The content of mineral pigment in such paints varies from 50% to 70% of the total. Linseed oil, together with a moderate percentage of drier and thinner, constitutes the vehicle. When such paints are applied to shingles, a very durable, water-proof film results. This film of dried paint upon the surface of a shingle has the effect of laying or smoothing down the rough, fuzzy surface of the wood, thus eliminating at once an important source of fire danger. The shingled dwelling upon which such paint has been used is practically rain-proof. It is, moreover, made very

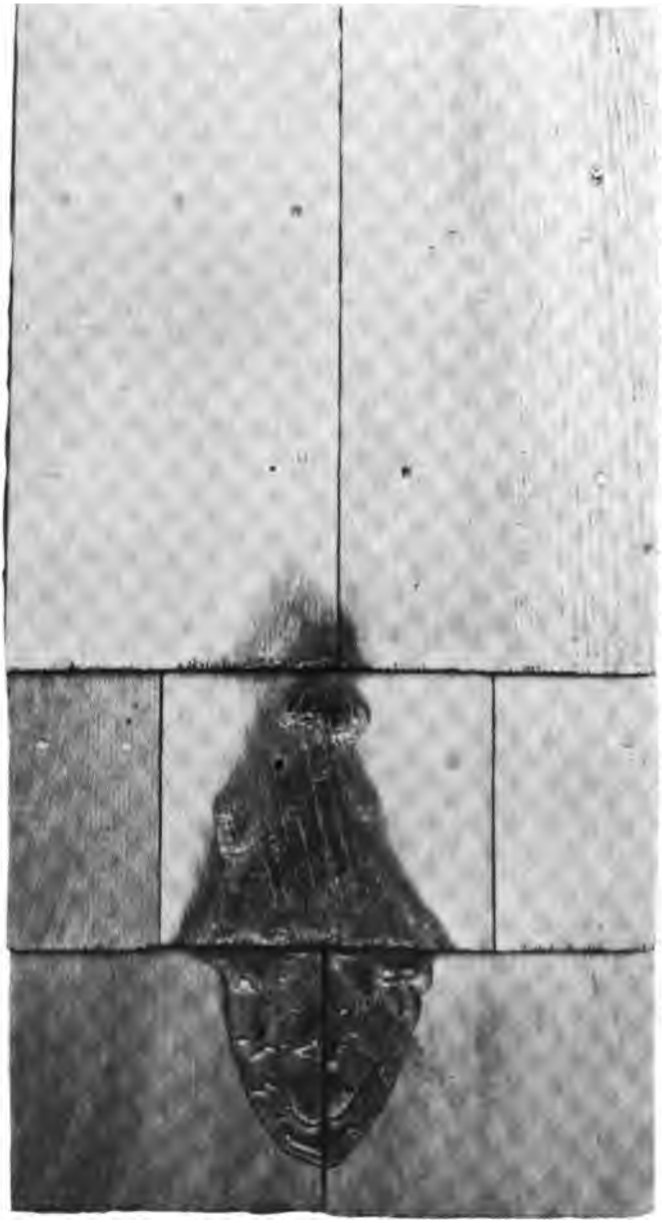

FIG. 97.
Effect of One-minute Torch Test on Untreated Shingles.

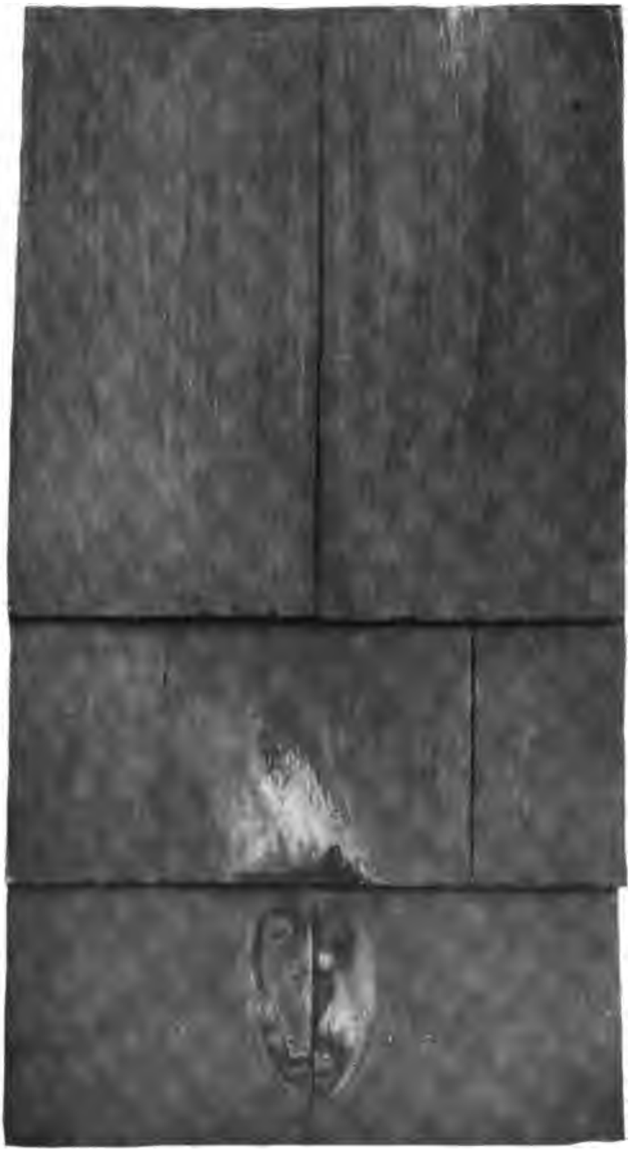

FIG. 98.

Effect of One-minute Torch Test on Painted Shingle.

attractive in appearance. Another important function is performed by the paint, in preventing the warping of shingles at the edge, thus doing away with the formation of pockets in which hot cinders might lodge and burn. The fourth and most valuable characteristic of high-grade paint is its resistance to fire. While the oil content is more or less combustible, there is present in the dried paint film a minor proportion of oil, the major proportion consisting of metallic and mineral pigments which are unaffected by fire. A hot cinder or spark, falling upon a roof properly treated with a high-grade paint, would, in most instances, roll from the roof to the ground. There would be no pockets in which to lodge and burn. In the event of hot cinders falling with great force upon relatively flat roofs, the cinders would probably lodge upon the surface and burn away the superficial coating of dried oil, gradually dying out as they reached the fire-resisting mineral pigment.

The writer has found that the best results are obtained by first dipping shingles in a mineral paint and later applying a brush coat of the same paint when the shingles have been laid on a roof. A very fire-retardant roof may thus be made. It is probable that the shingle manufacturer could easily do the dipping of the shingles in a large tank of paint well thinned. The shingles could pass out of the tank on an endless belt and through a set of rubber rolls in order to force the paint deeply into the wood and to remove the excess. They could then pass through a drying room and go direct to the bundling machines. Shingles thus painted with a good priming coat of fire-retardant shingle paint would doubtless prove readily acceptable to the builder.

At various times there have been placed upon the market fire-retarding solutions which have had more or less merit for the intended purpose. They consisted usually of water solutions of various salts, which when applied to canvas, scenery, or like materials, would dry and leave the material coated or impregnated with a quantity of the dried salts used in making the preparations. In treating wood or cloth with such salts, it was generally found necessary to apply several coats of solution, sometimes as high as six or eight,

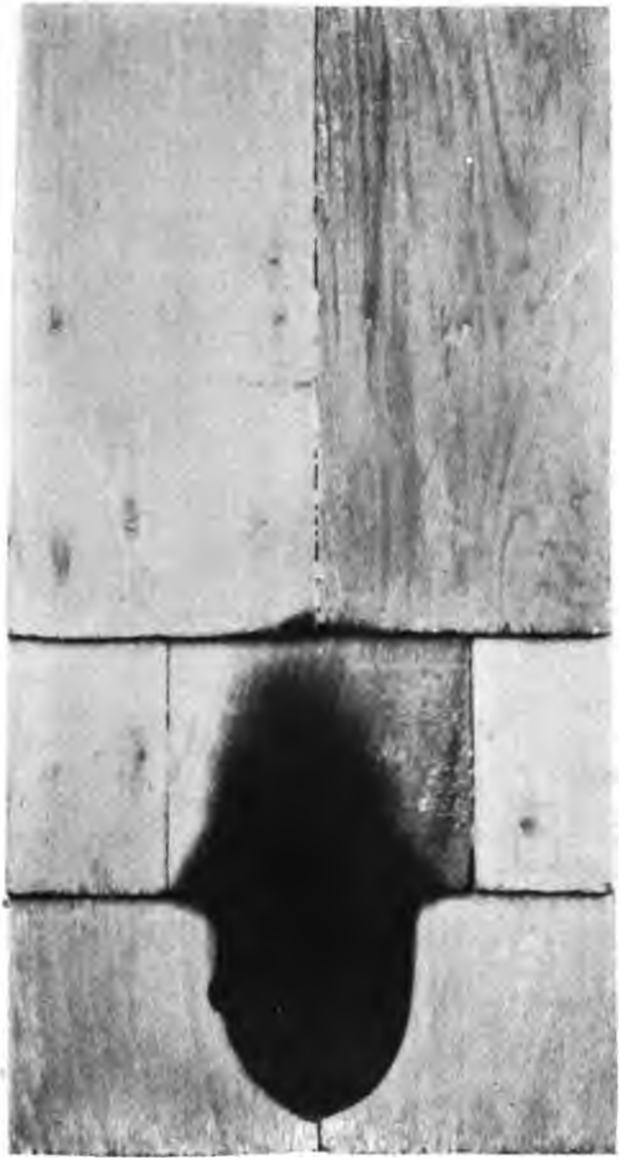

FIG. 99.

Effect of One-minute Torch Test on Shingles Mineralized with Common Salt.

in order to get satisfactory results. The chemicals used in many of these compounds are as follows: Ammonium phosphate, ammonium sulphate, ammonium chloride, sodium phosphate, calcium chloride, calcium oxychloride, calcium oxide, sodium carbonate, sodium chloride, borax, zinc chloride, zinc sulphate, etc. Sometimes the solutions contained casein or glue to give them binding or water-resisting properties when spread and dried.

It is obvious that the application of brush coats of any of the above-named salts to wooden shingles would not result in the formation of weather-resisting surfaces. It is possible, however, that a shingle manufacturer can at moderate cost impregnate shingles with certain mineral salts, which will make them more resistant to fire. Wooden beams and railroad ties are often rendered more durable by treatment with preservatives possessed of fungicidal properties, such, for instance, as creosote or zinc chloride. These chemical substances are forced deeply into the wood by pressure in treating cylinders. In the writer's opinion, it would be practical for the shingle manufacturer to adopt a similar process for mineralizing shingles. Mineral salts having a high resistance to fire could be used for the impregnation base. Shingles thus mineralized could be rendered still more resistant to fire by subsequently applying a coat of mineral paint. The writer has experimented with various salts for this purpose, and has treated shingles with solutions of them, both by brushing and by dipping. Shingles thus treated have shown much greater resistance to fire. The best results were obtained by mineralizing the shingles and subsequently coating them with mineral paint. The mineralizing process of making the wooden shingle thoroughly safe as a roofing material should be carried out in two steps. The shingle manufacturer should undertake the first process of treating the shingle with fire-resisting salts. If shingles thus impregnated are furnished the builder, it is quite certain that he will carry out the second and more important part of the process which consists in applying a decorative and waterproof coating of fire-resistant mineral paint. It will, of course, be possible to use the old-style creosote shingle stain over the mineralized

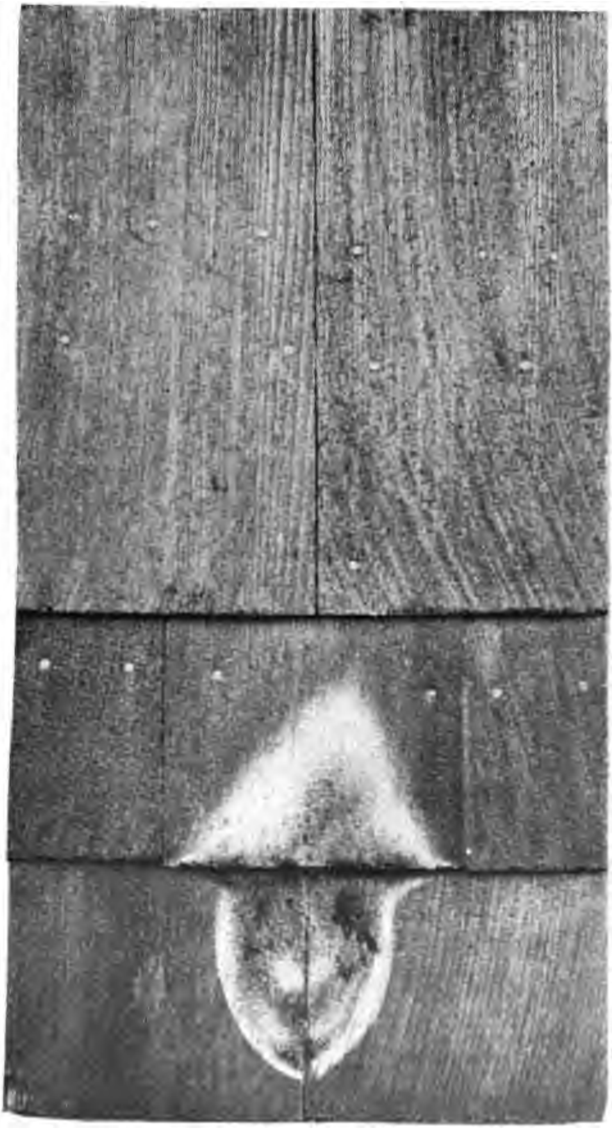

FIG. 100.

Effect of One-minute Torch Test on Shingles Mineralized with Alkaline Silicates.

shingle, in place of a mineral paint. However, the mineral paint will give much more satisfaction, as it forms a durable, waterproof film which is more resistant to fire than an ordinary stain.

There will probably be considerable inquiry as to what constitutes the best kind of fire-resisting mineral salts for use in impregnating shingles. While any one of those previously mentioned would prove of value, it is probable that a mixture of such salts as may be compatible will give the best results.

Exposure tests: Through the co-operation of Dr. Herman Von Schrenk, director of the laboratories of the Southern Cypress Manufacturers' Association, and Dr. Howard F. Weiss, director of the United States Forest Products Laboratory, several bundles of cypress and cedar shingles were obtained for test purposes. Some of these were treated with ordinary mineral paints, while others were treated with special types of fire-resisting paints. After three years' exposure those paints which were made with mineral pigment ground in linseed oil gave the best wearing values. The use of a small percentage of borax increased their fire-resisting characteristics.

Interior paints: Silicate of soda ground with mineral pigments produces a paint which dries to form a hard, heat-resisting surface. While such paints do not of themselves stand exterior exposure as well as a linseed-oil paint, they have been found quite satisfactory for use upon some kinds of interior surfaces. When applied to scenery, trim, or those fabrics which are not injured by alkali, the silicate paints are very successful as fire retardants. For use upon the interiors of warehouses, freight sheds, and other wooden structures where a fire-resistant coating is desired, they may also prove valuable.

Other uses for fire-resisting paints: The use of fire-retarding paints of either type will probably not be restricted to shingles. There are many structural materials upon which these products may ultimately find a wide use. For instance, they might be used to a considerable extent in treating different types of railroad equipment. Rail ties laid upon trestles are often destroyed by large red-hot cinders falling from the fire-boxes of passing locomotives. The mineralizing of such ties and subsequent treatment with fire-retarding paints will probably reduce such damage to a material extent. For factory decoration and equipment preservation, paints of a fire-resistant nature will find a wide application.

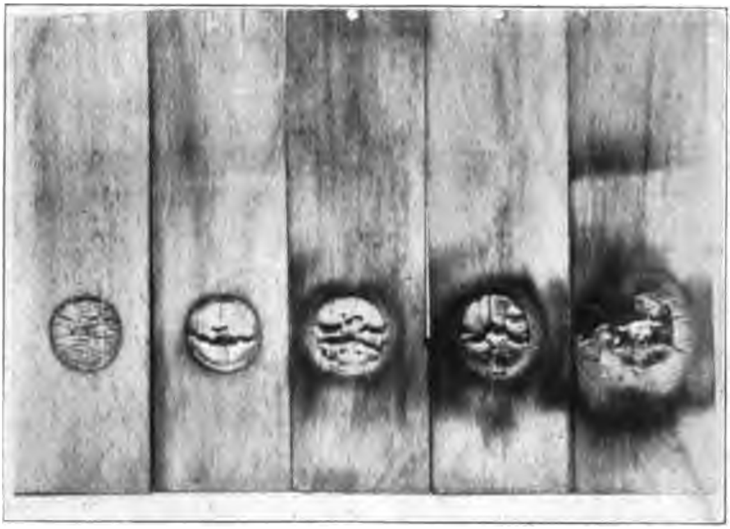

FIG. 101.

Effect of the Flame Test on Untreated Shingles A, B, C, D, and E at one, two, three, four, and five-minute flame exposures.

Testing paints: The writer, believing it desirable to have some standard by which to determine the fire-retarding nature of paints, made a search of various literature, in an effort to find tests outlined, which could be relied upon to give such data. Very little information along this line, however, could be obtained. In the book entitled "Fire Prevention and Fire Protection," by Freitag (John Wiley & Sons, publishers, New York City), pages 938 and 939, the following paragraphs appear:

"Fire-retarding Paints.—So-called 'fireproof' paints, or the cold-water compounds which are sold under a variety of trade names, all claiming fire-resisting properties, should be classed as fire-retardants rather than as fireproof. While

wood or other combustible materials which have been coated with such compounds will successfully withstand the blaze of a match, a few minutes' exposure to a greater heat, as of a lamp, will show that no great degree of fire resistance exists. However, the preventive value of such coatings is material, especially for scenery, properties, and other stage fittings, in that the quick spread or 'flash' of fire over such materials will be greatly retarded, if not altogether prevented. The use of fire-retarding paints or solutions is, therefore, to be strongly recommended for scenery, etc., whether required by law or not. Some cities, notably New York, require 'all stage scenery, curtains, and decorations made of combustible material, and all woodwork on or about the stage to be painted or saturated with some non-combustible material, or otherwise rendered safe against fire.'

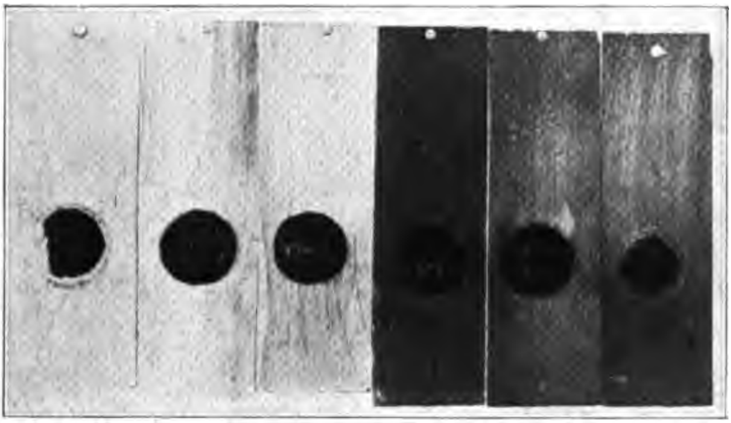

FIG. 102.

One-minute Flame Test Upon Shingles Mineralized by Coating with Solutions of Various Salts: 1, Alum; 2, Borax; 3, Sodium Sulphate; 4, Ammonium Phosphate; 5, Sodium Chloride; 6, Sodium Silicate.

"Acceptance of treatment depends on tests made by the Bureau of Buildings on the materials in each individual case.

"For fabrics, scenery, and the wood frames of same, there must be no flame or glow after the application, for fifteen seconds, of the flame of an ordinary alcohol lamp or torch.

"For paints, the following regulations are made:

"First. The term fireproof paint shall be understood to mean any preparation used to cover the surfaces of wood or other materials for the purpose of protecting the same against ignition.

"Second. No fireproof paint will be considered satisfactory unless it so protects the wood or other material to which it is applied that the same will not flame or glow after having been subjected to the flame of a gasoline torch for two minutes.

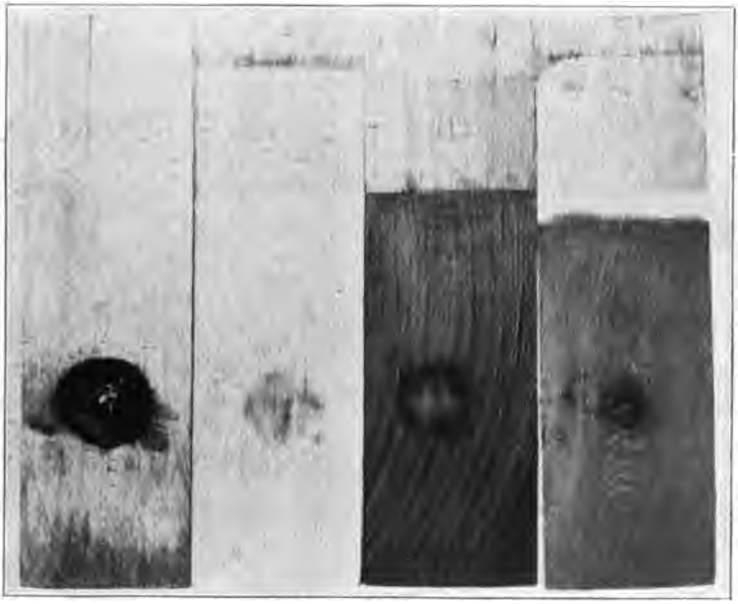

FIG. 103.

Flame Test.

Effect of flame upon shingles after one-minute exposure. A, unpainted; B, C, and D, painted.

"Third. Before applying fireproof paint to any material the surfaces must be cleaned.

"Fourth. Application of fireproof paint must be repeated whenever it is found that the material to which it is applied is no longer protected to fulfil Specification No. 2."

It is probable that the severe two-minute gasolene torch test outlined above was designed to be used upon paint coatings applied to thick trim. It is improbable that such a test

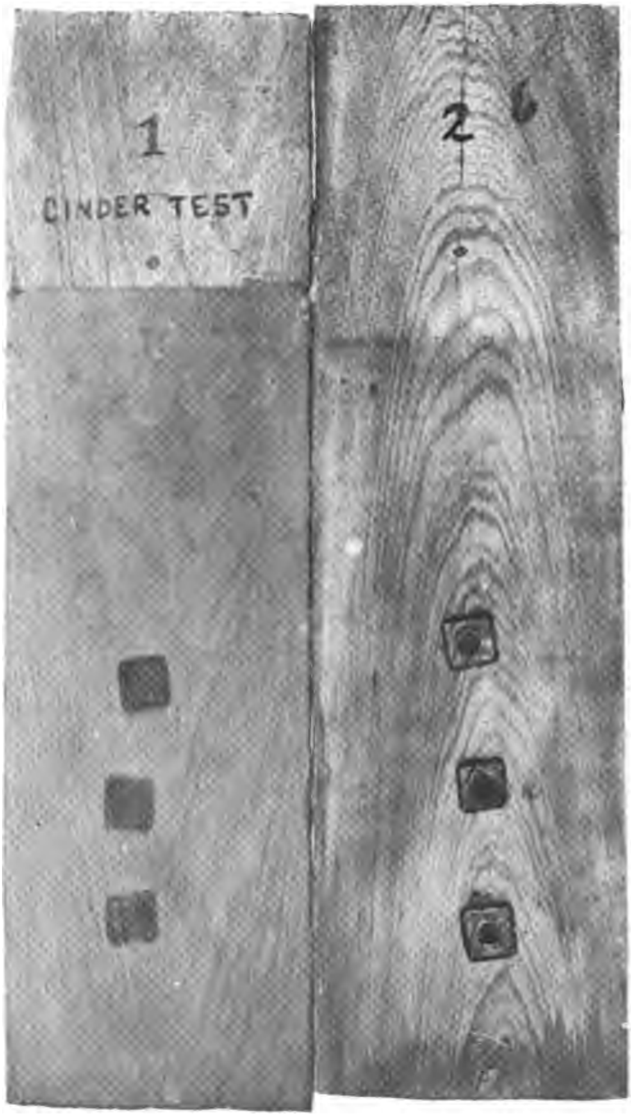

FIG. 104.
Effect of Cinder Test on Painted Shingle No. 1, and Untreated Shingle No. 2. Note Deeply Charred Surface of Untreated Shingle.

could be withstood by a shingle painted with the most resistant of paints, or even coated with a thin sheet of metal. The thin shingle, with its content of resins or oil, would probably carbonize, although the surface coating might be unaffected. To demonstrate this, the writer applied to several shingles a slush coating of neat Portland cement ⅛ inch thick. Another set of shingles was painted with a paint containing Portland cement as the pigment. After setting for three days, the coated shingles were subjected to a one-minute torch test. The fire-resisting effect of the Portland cement coatings was no better than that shown by a high-grade linseed-oil-mineral oxide paint. The writer has therefore devised a series of tests to

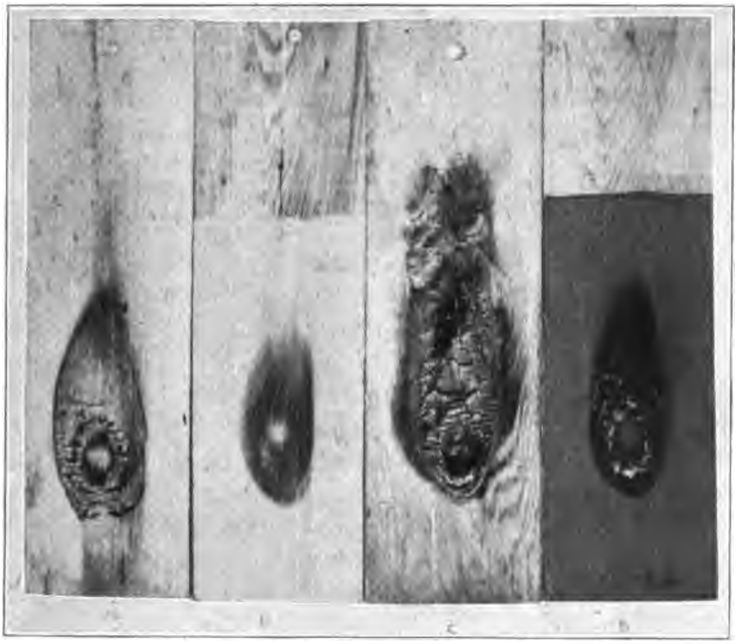

FIG. 105.

Torch Tests.

Effect of torch on untreated shingle A and painted shingle B at end of one-minute test. Effect of torch on untreated shingle C and painted shingle D at end of three-minute test. Note effect of paint in preventing spread of fire and retarding the charring of the wood.

determine the suitability of paints as fire-retardants. These tests are, of course, only offered as preliminary or tentative tests, for the study of testing engineers interested in the subject.

Methods of Testing Fire-retarding Paints.

Flame Test.—The test will be made upon an open tripod approximately 9 inches in height, the ring top being about 3½ inches in diameter. Upon the top of the tripod is placed a 12-inch square of asbestos board ⅛-inch thick. In the center of the board there should be a 3-inch hole directly over the tripod opening. The shingle to be tested shall be placed directly over the center of the opening and in such position that its lower portion shall be flush with the edge of the asbestos board. A (one kilo) weight is placed upon the shingle, approximately at points corresponding to the edge of the opening in the asbestos. Under the tripod shall be placed a Bunsen burner so regulated that the tip of the flame will just reach the shingle. The shingle shall be allowed to remain there for one minute, subjected to the action of the flame. Upon removal, the shingle must not burn or show a glowing surface or a deeply checked or charred condition of the wood. For comparison, a blank test may be made with an untreated shingle of the same grade and kind of wood.

Torch Test.—A shingle shall be placed with the shank edge resting upon a tripod, the butt upon the table, at an incline of approximately 45°, thus corresponding to the position in which it would be placed upon a roof. A Bunsen burner shall be placed in a horizontal position, with the top within ½ inch of the shingle at a point 5 inches from the butt. The free flame of the burner shall be allowed to strike the shingle. At the end of one minute the flame shall be removed. Painted shingles shall not show any deeply checked or charred condition of the wood below the paint. Blank tests should be made with untreated shingles of the same wood, for comparison and to determine the efficiency of the paint.

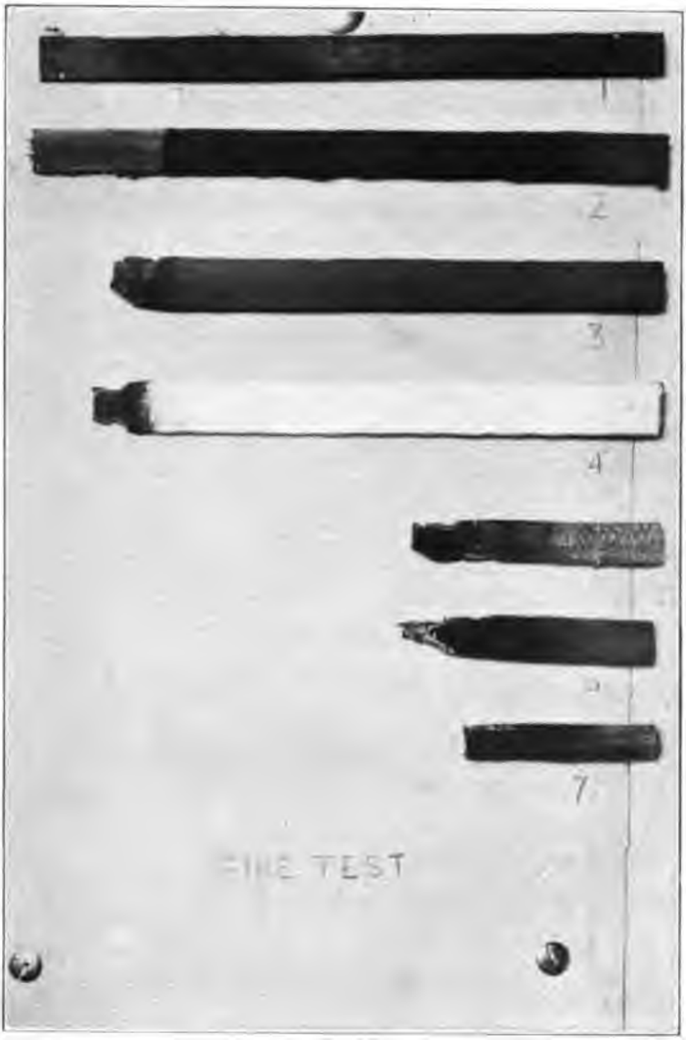

Fig. 106.

Fire Test.

Effect of Fire Upon Shingle Strips.

No. 1, untreated, and No. 2 were not subjected to the test. Nos. 5, 6, and 7 are strips of untreated shingles, showing effect of test. No. 3 and No. 4 were painted. Note effect of paint in preventing the combustion of the shingle strips.

Cinder Test.—For this test there will be required an iron nut of approximately the following dimensions: 13/16 inch square, height 7/16 inch, bore ½ inch. The nut shall be placed upon iron gauze resting upon a 9-inch tripod, and subjected to the free flame of a Bunsen burner for two minutes. The nut shall be removed with a pair of tongs, and immediately placed with its flat side upon the shingle under examination. A lighted match is to be applied at five-second intervals to the edge of the threaded portion of the nut. There must not be shown any permanent blaze due to combustible gases evolved from the wood. A blank test should be made upon an untreated shingle. The nut must not cause the formation of any deeply checked or charred surface condition of the wood beneath the paint.*

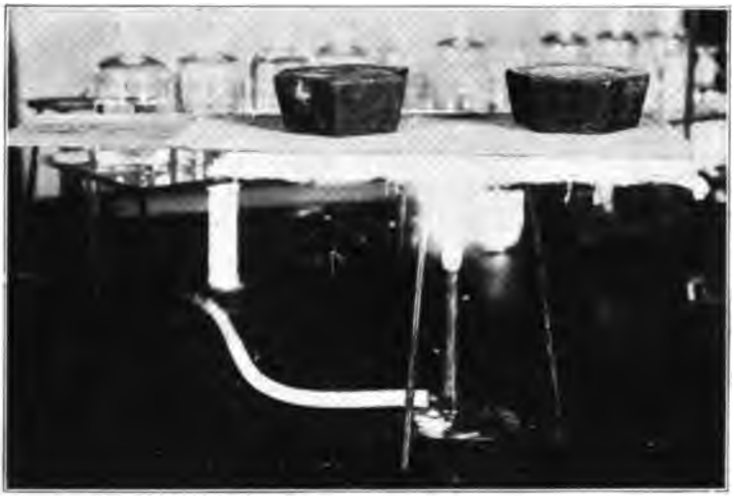

FIG. 107.

Method of Conducting the Flame Test Upon a Painted Shingle.

Fire Test.—Cut from the center of a shingle with a saw several small strips. That portion of the shingle should be selected which will allow of the strips being of approximately the following dimensions: Thickness of upper edge, 3/16 inch; thickness of lower edge, 5/16 inch. The strips should be approximately ⅝ inch in width and approximately 8 inches in length. Nine of such strips may be prepared from a 6 x 20 shingle, if the wood is uniform and free from defects.

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* This test has not been found to give concordant results.

These shingle strips or "matches" should be given either a dipping or heavy brush coat of the paint under test. The upper edge of the strip, for a space of 1¼ inches, should be left unpainted. After allowing 48 hours for the thorough drying of the paint, the strip should be held by the thick, painted lower edge in a horizontal position. The thin, unpainted upper edge should be placed in the free flame of a Bunsen burner, and ignited so that it burns freely when withdrawn. The strips should be kept in a horizontal position, but occasionally may be revolved by turning the fingers so that the flame will have a good opportunity to reach every portion of the untreated wood. When the flame reaches the painted portion of the wood, it must die out and not have any appreciable effect thereon. A blank test may be carried out with an unpainted strip.

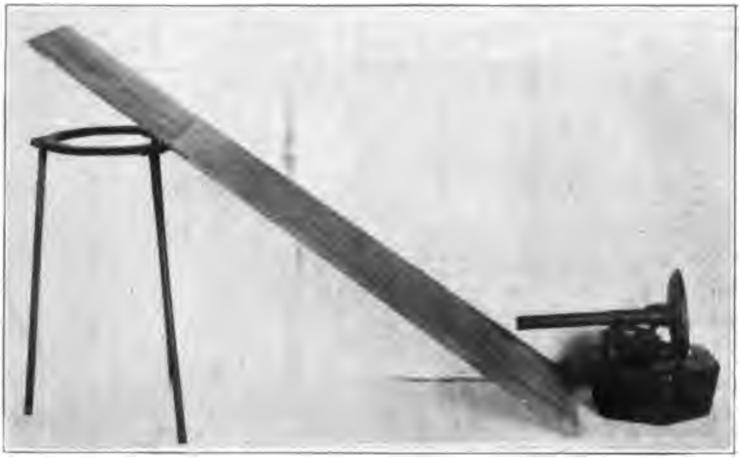

FIG. 108.

Method of Conducting the Torch Test Upon a Painted Shingle.

Of the above outlined tests, the Torch Test is probably the most practical.

Table 16.*

Test C.

Results of Inflammability Test on Treated Cypress Siding.

Treatment	Number of Shingles in Average	Average Temp of Plate When Specimen Was Placed	Average Time of Exposure to Heating Plate				Average Duration of Burning after Removal		Remarks
			Before Igniton		After Ignition				
		°C.	Min.	Sec.	Min.	Sec.	Min.	Sec.	
Natural cypress.......	3	325	1	8	..	..	9	5	Burned violently; all but lower unexposed portion consumed.
6% solution ammonium phosphate di basic	3	325	12 minutes without ignition				Did not burn		Flashing occurred several times. No steady ignition. Pieces were glowing after 5′ exposure. The pieces were exposed 12′.
10% solution ammonium sulphate....... .	3	325	12 minutes without ignition				Did not burn		Flashing of small blue flame occurred; at no time did the specimens blaze up.
10% solution sodium borate..............	3	325	12 minutes without ignition				Did not burn		The pieces of this treatment ignited and burned about 30″, when the flame went out. The pieces could not be ignited until the specimen was all aglow, when a small blue flame burned over the glowing portion. These specimens were charred through.
3% am. phosphate, 5% am. sulphate mixture	3	325	12 minutes without ignition				Did not burn		Flashing occurred at times. No steady burning occurred.

*Bulletin, National Fire Protective Association.

TABLE 17.*

Cost of Impregnation and Painting.

Chemical Fire Retardant	Estimated Absorption of Preservative by (1,000) 4 Bundles of Red Cedar Shingles.		Cost per Pound of Chemical.	Estimated Cost of Chemicals to Fireproof 1,000 Shingles.	Estimated Cost of Paint Necessary to cover ¾ of (1,000) Shingles Both Sides.	Total Cost of Chemicals and Paint necessary to Fireproof 1,000 Red Cedar Shingles.
	Pounds Solution.	Pounds Dry Salt.				
4% solution ammonium phosphate di basic..........	266	10.64	$0.0875	$0.94	$1.40	$2.34
7% solution of ammonium sulphate.	266	18.62	.035	.65	1.40	2.05
3% ammo. phosphate } mixture		7.98	.0875			
4% ammo. sulphate } mixture	266	10.64	.0350	1.08	1.40	2.48
8% sodium borate (borax)..........	266	21.28	.0375	.80	1.40	2.20
Zinc borate using 3% solution of zincchloride, 10% solution of borax‡.	266	7.98 26.60	.0350 .0380	1.29	Not necessary	1.29
Mixture of 7½% ammo. alum and 7½% aluminum sulphate.........	266	19.95 19.95	.020 .010	.60	1.40	2.00

*Bulletin, National Fire Protective Association.

Summary of Conclusions.

The shingled roof is highly desirable on account of its durability, light weight, low cost, and non-conducting properties.

Shingled roofs are subject to conflagration when they become dry. Hot cinders from chimneys or glowing sparks carried by the wind from near-by fires, are common causes of roof fires.

The use of high-grade mineral paints upon shingled roofs eliminates such fire danger. Shingled structures of all types, when properly painted, are not only fire resistant, but they are moisture proof and highly ornamental.

Shingle makers should put on the market shingles that have been impregnated with a priming coat of fire-retardent paint made of mineral pigments ground in a linseed-oil vehicle.

The painted shingle dwelling constitutes one of the most desirable types of modern suburban homes.

Wooden structures of all kinds are preserved for years, and made resistant to fire, through the application of suitable paints.

N. F. P. A. Tests: Considerable data on the subject of the fire-resisting properties of impregnated shingles is given in Tables Nos. 16 and 17 recently published in the Bulletin of the National Fire Protective Association.*

The general conclusions from these tests as published by the National Fire Protection Association are given in the following summary:

"*General Conclusions.*

"From a consideration of all of the data given in this report it appears that:

> "1. There was very little variation in the inflammability of the various species of untreated woods when tested at the higher temperatures. For example, all of the specimens tested at 375 degrees C. ignited within two minutes.
>
> "2. Ammonium salts and sodium borate gave more efficient results than the other chemicals tested in rendering wood fire retardant. All of the other salts tested either did not prevent free combustion of the wood when injected in moderate quantities or they reacted with the wood, weakening and discoloring it.
>
> "3. None of the chemical fire retardants used, when injected into the wood, prevented it from glowing or charring.

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* Report of the Committee on Uses of Wood in Building Construction.

"4. Wooden shingles may be rendered fire retardant by injecting certain chemicals. The additional cost of painting which is necessary with water soluble salts would, in most cases, no doubt, restrict the use of such treatments.

"5. The use of insoluble metallic borates precipitated in shingles appears to be the most practical of the methods studied for rendering wooden shingles fire retardant.

"6. All of the paints tested with shingles rendered them to some degree more fire retardant. The most effective of the paints tested which were suitable for outside use was one containing zinc borate pigment which acted as a fire retardant.

"7. Shingle stains of the type tested did not greatly increase the inflammability of the shingles, even though they were applied shortly before being tested. Their use as a means of decorating treated shingles should, no doubt, be allowed, as they do not detract materially from the fire-retarding treatment.

"8. The paints tested which were designed for interior use were in general more effective than the paints designed for outside use in retarding fire.

"9. The method of application of a paint is of considerable importance. It would seem to be good practice with shingles to apply the paint to approximately three-fourths of both sides before laying the shingle."

CHAPTER XIV.

THE COMPOSITION OF PAINT VAPORS.

Freshly painted surfaces give to the surrounding air a peculiar odor. In closed rooms this odor is pronounced and easily recognized. Painters are in the habit of stating that the vapors of fresh paint have a "leady smell." This is probably due to the fact that white lead is used as the base upon which the majority of paints are prepared. The painter has therefore always associated this pigment with the characteristic odor of fresh paint. Some cases of illness among painters have been ascribed to the effects of paint vapors. People occupying freshly decorated sleeping rooms, which are not well ventilated, have at times complained of illness from the same cause. E. C. Baly* examined spectroscopically the vapors from basic carbonate-white lead paint, and found evidences of metallic lead therein. The vapors from basic sulphate-white lead paint or zinc oxide paint, when examined in a similar manner, showed the absence of metallic constituents. Some cases of lead poisoning among painters could be ascribed to the vapors from basic carbonate-white lead paints, if lead compounds could actually be found present in such vapors. Armstrong and Klein,† after conducting an elaborate series of tests, concluded that lead is not present in the vapors from white lead paint, but that the toxic effects produced by such vapors are due almost entirely to the volatile substances given off by the turpentine present.

The writer has made a series of tests which confirm those of Armstrong and Klein, in so far as their results are concerned with the non-metallic constitution of paint vapors. The writer's tests, however, show that the vapors from paint apparently contain carbon monoxide, the poisonous nature of which is too well known to be commented upon. The amount of carbon monoxide evolved is also shown to be directly influenced by the type of pigments used in the paint. The definite presence of aldehydes and organic acid substances in paint vapors has also been established by these tests. The data presented has brought forth considerable information regarding the phenomenon of oxidation as applied to linseed oil and linseed oil paints. The results are given with a view to awakening further research work of a similar nature. An outline of the tests made is herewith presented, together with a summary of the results obtained and in some instances a discussion of the data. Many of the tests outlined were made in duplicate.

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* *The Oil and Colour Trades Journal,* May 6, 1911, p. 1518.
† *J. S. C. I.*, 32, 320 (1913).

Experiment I.—Four cylinders each 30 in. long and 9 in. in diameter, were formed of galvanized sheet iron. One end of each cylinder was fitted with a removable lid. The other end was closed. The seams were all soldered. The tanks were numbered from 1 to 4. The interiors of the tanks were brush-coated with raw linseed oil, soya bean oil, tung oil, and menhaden oil, respectively. The tanks were weighed previous to and subsequent to the application of the oil, in order to determine the amount of oil applied. The tanks were individually connected up to a train of three Woulff bottles, the first of which contained 66° sulphuric acid, the second and third containing a saturated solution of barium hydrate. Vacuum was applied to the end bottle. The air entering the tank was scrubbed through a 10 per cent. solution of caustic soda, and then passed over soda lime to eliminate carbon dioxide.

Soon after the tests were started, the sulphuric acid in the first bottle of each train became discolored. Within an hour the acid had assumed an amber color. The barium hydrate contained in the other bottles became opaque within a short time. At the end of a 2-day run, the sulphuric acid was dark red, and the barium hydrate solutions contained a dense white precipitate which proved to be barium carbonate. Each series of apparatus was disconnected and the coatings on the interior of the tanks examined. The amount of air passing through the tanks in 2 days was evidently insufficient to complete the oxidation of the oils which under normal conditions would have been quite dry in that time. The linseed oil was very soft and tacky. The soya bean oil was but slightly oxidized. The fish oil was somewhat tacky, but it had dried to a greater extent than the other two oils mentioned. The tung oil was very hard and dry. The smell emanating from the tanks was most unpleasant, being somewhat characteristic in each instance of the type of oil used. A certain nauseous smell, however, was common to each tank. The discolored sulphuric acid from each test had an acrid odor. The bottles containing barium carbonate had an odor suggestive of aldehydes.

Results.—These tests indicate that the phenomenon of oxygen absorption which takes place when oils are spread in thin layers and exposed to the air, is accompanied by the evolution of considerable amounts of organic substances. Large quantities of carbon dioxide are simultaneously evolved.

Experiment II.—A series of paints was prepared from those opaque white pigments which are most widely used in the manufacture of exterior and interior paints (basic carbonate-white lead, basic sulphate-white lead, zinc oxide, and lithopone). The oil used was raw linseed oil. No turpentine or drier was added. The lead pigments were ground to a thick paste with 10 per cent of oil. The zinc pigments were ground to a paste with 15 per cent of oil. Oil in the proportion of about 7 gals. to the cwt. of paste was then added to each paint, the quantity of oil added in each instance being sufficient to make paints containing approximately 60 per cent pigment and 40 per cent oil. Each of the four iron cylinders described in Experiment I was then cleaned and painted on the inside with one of the four paints. An effort was made to spread the same amount of paint in each tank. After painting, the tops were placed upon the tanks and they were connected up to Woulff bottles containing various reagents, as shown in Fig. 55. Uniform vacuum was applied to the end of each apparatus, and a 48-hour run was made. The air passing into the apparatus was scrubbed through a 10 per cent solution of caustic soda and then passed over soda lime in order to remove the carbonic acid present. The glass tubes coming from the ends of the cans were bent as shown in the illustration, to hold back any particles of paint which might be carried over, although such occurrence seemed highly improbable and such precautions unnecessary. A part of each exit tube was heated with the flame of a Bunsen burner, in order to break up, if possible, any organic form of lead or zinc, which might be present in the vapors, since certain organic compounds of lead may not respond to tests for lead as made with ordinary reagents.

In every test the sulphuric acid contained in the bottle next to the tank was turned amber color within 5 minutes after the beginning of the test, thus showing that the drying paints were giving off considerable organic matter. After a 48-hour run, the acid in each bottle was dark red. The amount of carbon dioxide evolved in each test was considerable. No quantitative determination of carbon dioxide was made in any case. At the end of the experiment, the cans were re-weighed to determine the amount of oxygen absorbed. To the writer's surprise, there was recorded a loss of weight in one test, and but slight, if any, gains in the other tests. The basic carbonate-white lead paint lost 2 per cent by weight. The basic sulphate-white lead paint and the zinc oxide paint neither gained nor lost, the weight of the films remaining constant. The lithopone paint showed less than 1 per cent gain.

The bottles containing the sulphuric acid were removed from each train and the contents examined. Upon dilution with water, the acid in the bottle, through which the fumes from the drying basic carbonate-white lead paint had been passed, became opaque. It was at first thought that this cloudiness of the diluted acid might be due to the presence of lead sulphate, formed by the absorption of volatile lead compounds eliminated by the drying paint. Alcohol was added to a portion of the liquid. It immediately became clear, thus indicating the absence of lead. A very thorough examination of the liquid was then made, and not a trace of lead was found. The sulphuric acid through which the vapors from the other paints were passed, was also examined. No metallic compounds were

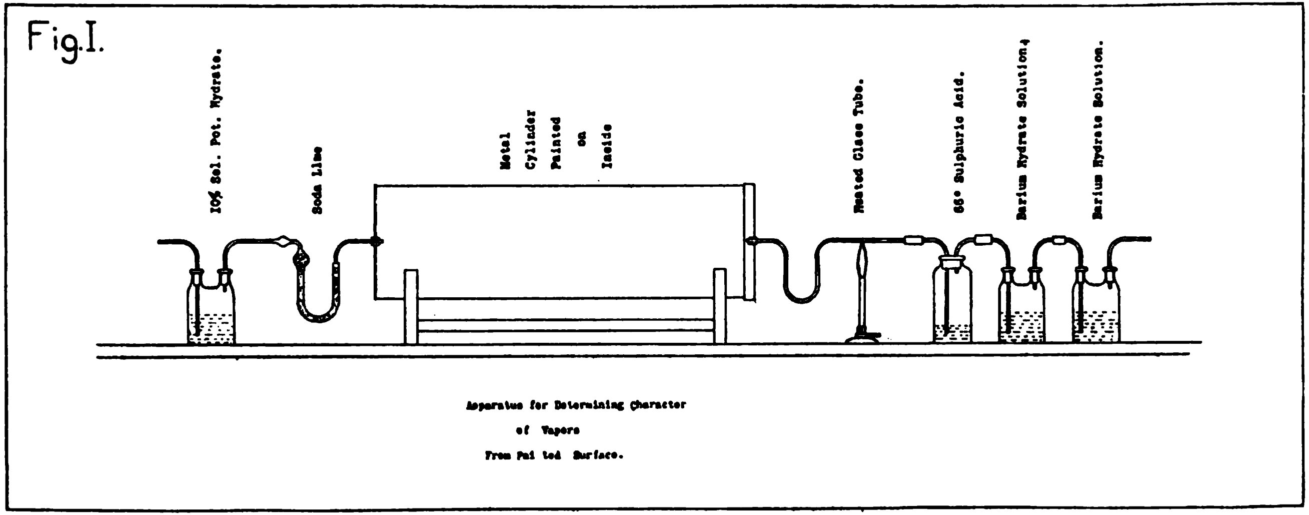

FIG. 109.

APPARATUS FOR DETERMINING CHARACTER OF VAPORS FROM PAINTED SURFACES.

1—Solution KOH, 10 per cent.
2—Soda Lime.
3—Metal Cylinder Painted on Inside.
4—Heated Glass Tube.
5—Sulphuric Acid 66°.
6, 7—Barium Hydrate Solution.

found. The experiments were repeated, the only refinement being that of introducing in front of the sulphuric acid bottles in the trains connected to the lead-painted cylinders, a bottle containing strips of filter paper saturated with sodium sulphide solution. The papers were not darkened in either case, thus giving further indication of the absence of lead compounds. In another experiment, one of the cylinders was painted with basic carbonate-white lead paint and the gases evolved were passed through a heated tube, finally being drawn through a 2 per cent solution of nitric acid. The test was run for forty-eight hours. The acid was evaporated on a steam bath. The residue was taken up with dilute acetic acid and a few drops of water. It was tested microscopically* for lead after the addition of copper acetate and potassium nitrate. No response for lead was shown in the test.

Results.—The results of these tests indicate that drying paints, containing zinc or lead pigments, do not emit volatile compounds of a metallic character.

When spread as thin films, oil-pigment paints are capable of evolving considerable amounts of organic substances without showing any material increase in their respective weights.

Experiment III.—Experiment II was repeated after cleaning the interior of the tanks and applying fresh coats of paint. The first Woulff bottle in each train contained distilled water. The second bottle contained 66° sulphuric acid. After a 48-hour run, the contents of the first bottle in each train were examined. The water in each instance was acid in reaction. There were required for neutralization from 1 cc. to 14 cc. of $N/10$ KOH. The water in the bottle connected to the cylinder painted with lithopone showed the lowest amount of acid, while the water connected to the cylinder painted with basic carbonate-white lead showed the largest percentage of acid. The presence of carbon dioxide in the water may partially account for the acidity of these tests. A portion of the neutralized acid was tested qualitatively for the presence of aldehydes. Small amounts of aldehydes were

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* Page 167, "Lead Poisoning and Lead Absorption," Legge and Goadby. Longmans, Green & Co., Publishers.

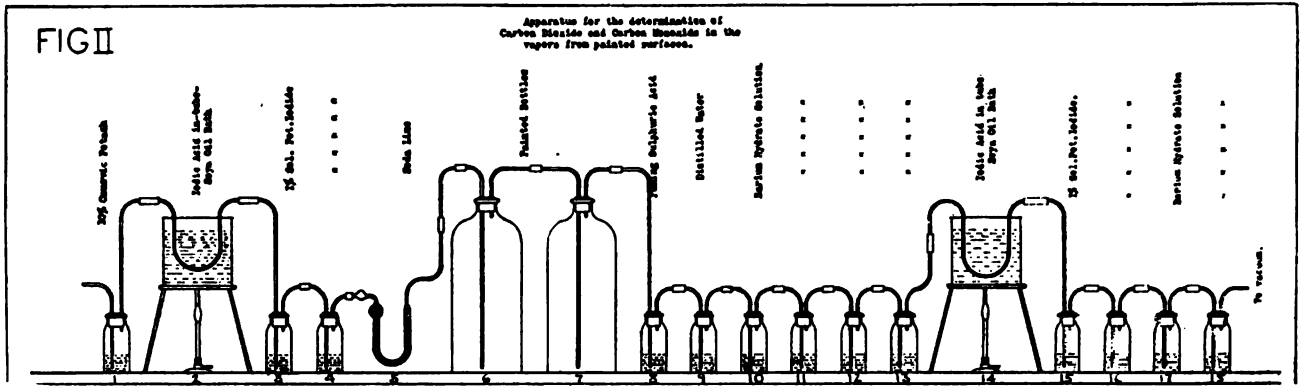

FIG. 110.

APPARATUS FOR DETERMINATION OF CO_2 AND CO IN VAPORS FROM PAINTED SURFACES.

1—Solution KOH, 10 per cent.
2, 14—Iodic acid in tube, Soya Oil Bath.
3, 4, 15, 16—1 per cent KI Solution.
5—Soda Lime.
6, 7—Bottles Painted on Inside.
8—Fuming Sulphuric Acid.
9—Distilled Water.
10-13, 17, 18—Barium Hydrate Solution.

found present. Formates were also found present. The sulphuric acid in each of the four bottles was diluted with water and titrated with $N/10$ potassium permanganate to determine the amount of reducing substances present. The acids in the trains connected to the cylinders painted with white-lead paints each required about 100 cc. permanganate solution. The acids in the trains connected to the cylinders painted with zinc paints required from 19 to 39 cc. of permanganate, that connected to the lithopone cylinder requiring the least amount. The solutions of acid thus oxidized were transferred to separatory flasks and shaken with ether. The ether solutions were thoroughly washed with water and then evaporated. In each instance a dark substance which had the appearance of heavy oil was left as a residue. This substance was found to be soluble in alchol, in which solvent very acid reactions were given. No attempt was made to identify the acids present. Their complex nature would make such determination rather difficult, especially when working on small quantities.

Results.—1. The above experiments indicate that the vapors from drying paints contain acids of a water-soluble nature. These acids apparently contain formic acid. The amount of such acid evolved may be influenced by the type of pigment present in the paint. The basic pigments are apparently more active than the neutral or inert pigments.

2. Organic acids of a fatty or aromatic nature are apparently evolved from drying paints. The amount evolved may bear some direct relation to the pigment present in the paints. The basic pigments apparently are most active in this respect.

The aldehydic reducing substances and the acids which are evolved from paints are, no doubt, responsible for the odors which are coincident to the drying of paints. In the writer's opinion, however, there are also evolved substances of a more poisonous nature. Inasmuch as large percentages of carbon dioxide are formed, it is at least possible that carbon monoxide may also be produced. The following experiments were designed to determine whether this gas is really formed.

Experiment IV.—After many attempts to devise a suitable apparatus in which to determine the percentage of carbon dioxide or carbon monoxide which might be evolved by drying paints, the apparatus shown in Fig. 110 was found to be most satisfactory for the purpose. The first experiment made with this apparatus was conducted upon raw *linseed oil.* The interiors of two carefully weighed glass bottles, each having a capacity of one gallon, were coated with linseed oil. The oil was poured into each bottle and allowed to flow over the entire area of the interior, this being accomplished by revolving the bottle. After draining out the superfluous oil, the bottles were re-weighed to determine the amount of oil used for the test. Cork stoppers carrying glass air-tubes, were then inserted. The stoppers were thickly coated with paraffin to make them air-tight. The apparatus was connected up as shown in Fig. 110. Vacuum was applied at one end. As the purpose of the experiment was to determine the presence and amount of carbon dioxide or carbon monoxide in the vapors from the oil, the air entering the bottles was first freed of its content of carbon dioxide and carbon monoxide. This was accomplished by first scrubbing it through a solution of caustic soda in order to remove the carbon dioxide. The air was then run through a U-tube containing iodine pentoxide heated in a bath of soya oil to 150° C. at which temperature carbon monoxide is oxidized to carbon dioxide.* The iodine liberated was absorbed in a 1 per cent solution of potassium iodide and the carbon dioxide formed was taken up by the caustic soda and soda lime in the subsequent train of apparatus.

After the tests had been running for 15 minutes, the fuming sulphuric acid in bottle 8 was turned amber color, showing that organic substances evolved by the oil were being absorbed.

The absorption of these organic vapors by the sulphuric acid prevented such vapors from interfering with the subsequent train of liquids in which the percentage of carbon dioxide and carbon monoxide were to be determined. Bottle 10 containing saturated barium hydrate, the strength of which was determined by titration, showed a slight precipitate of barium carbonate at the end of the first 10-minute run. At the end of a 5-hour run, bottles 10, 11 and 12 showed quite a noticeable deposit of barium carbonate. Bottle 15, containing potassium iodide, did not change color until the tests had been under way for over an hour. At that period the reagent became slightly yellow, showing that some iodine had been carried over into this bottle, thus indicating the presence of carbon monoxide in the vapor. The barium hydrate in bottle 17 at the same time became cloudy, showing that traces of carbon monoxide which had been evolved, had been oxidized and absorbed as carbon dioxide. The percentage of carbon monoxide evolved by the drying oil in five hours was determined by titrating the barium hydrate contained in bottles 10 to 13 with $N/10$ oxalic acid, using phenolphthalein as an indicator. The titration was made direct. The amount of carbon dioxide found present was 0.016 per cent. The amount of carbon monoxide was not measurable, although it was shown to be present in traces.

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* "Method Used for Examination of Tunnel Gas," by Dr. A. Seidell, Hygienic Laboratory, Washington, D. C.

Results.—This experiment indicates that linseed oil in drying gives off traces of carbon monoxide.

Experiment V.—Experiment IV was repeated, coating the interior of the bottles in this case with basic carbonate-white lead paint in place of raw linseed oil. The test was run for five hours. The amount of carbon dioxide produced in that time was 0.0305 per cent. The carbon monoxide evolved amounted to 0.006 per cent. The experiment was made with basic sulphate-white lead paint in place of basic carbonate-white lead. The experiment was accidentally interrupted.

The experiment was again repeated, using zinc oxide paint in place of the white lead paint. The amount of carbon dioxide evolved was 0.0292 per cent. The amount of carbon monoxide evolved was 0.0039 per cent.

The experiment was again repeated, using lithopone paint in place of the zinc oxide paint. The amount of carbon dioxide evolved was 0.022 per cent. A mere trace of carbon monoxide was found.

Experiment V was repeated with a basic carbonate-white lead paint. The first bottle leading from the painted bottles contained fuming sulphuric acid to intercept and collect the organic vapors. The second bottle contained water. The third bottle contained alkaline bisulphite solution to collect any traces of aldehydes which, if evolved by the paint, might possibly escape absorption by the sulphuric acid. The fourth and fifth bottles contained water and caustic soda solutions, respectively, the latter to collect the carbon dioxide or phenols evolved. The vapors passing from the last bottle were passed through a U-tube containing small lumps of caustic potash. The U-tube was immersed in hot soya oil. At the end of a 5-hour test, the U-tube was removed from the hot oil and the lumps of caustic potash removed and examined for the presence of formates which, if present, would indicate that absorption of carbon monoxide had occurred. After dissolving the potassium hydrate in water, making acid with tartaric acid and distilling over barium carbonate suspended in water, the filtrate from the barium carbonate was treated with a small percentage of bichloride of mercury. After the solution had stood over night, a very faint precipitate of calomel was observed, indicating the presence of carbon monoxide.

Results.—These experiments would tend to show that the highly basic pigments stimulate the evolution of organic substances from linseed-oil paints, especially influencing the amount of carbon dioxide and carbon monoxide evolved.

The amount of air entering the painted bottle in a 5-hour run was insufficient to cause any marked oxidation. This explains why such small amounts of carbon dioxide and carbon monoxide were obtained. The extremely small quantities present made the analytical determinations a matter of great care. Tests extending over a greater period should be made, in order to substantiate the figures presented. The writer is designing another type of apparatus in which it is hoped more accurate determinations may be made.

Experiment VI.—In this experiment a portion of lithopone paint was reduced with 15 per cent of turpentine and then applied to the interior of the bottles. At the end of three hours, the percentage of carbon dioxide evolved was 0.04, while the percentage of carbon monoxide was 0.003. This result may be due to the oxidation of the turpentine.

Results.—Turpentine apparently accelerates the reactions which are responsible for the formation of volatile products from drying oils. The oxidative properties of the turpentine are probably responsible for this result.

General Discussion of Results.

The results obtained in Experiment II, in which the paint films showed but slight if any increase of weight at the end of the tests, are interesting. They may be partially accounted for by assuming that the amount of air passed through the tanks in 48 hours was very small. It will be well at this point to discuss the experiments on linseed oil and oil-pigment paints, as made by Sabin.* He describes a series of tests in which various paints were applied to small glass plates, the increase in weight shown by the paints being recorded at different periods. At the end of 7 days, raw linseed oil showed a gain in weight of 18 per cent, while white lead paint showed a gain of approximately 15 per cent.

The writer carried out a similar series of tests with a set of paints made up with 60 per cent of pigment and 40 per cent of raw linseed oil. The gain in weight of the films at the end of 7 days was as follows:

	Per cent.
Linseed oil	14.0
Corroded white lead	6.4
Sublimed white lead	7.1
Zinc oxide	5.4
Lithopone	5.9

These tests indicate that oil-pigment paints do not gain in weight to the same extent as raw linseed oil. Heretofore, however, investigators have not give consideration to the possibility that pigments may stimulate not only those processes which cause the oil to increase in weight through the absorption of oxygen, but also those processes and reactions which cause the oil to eliminate volatile substances, which might detract materially from the weight of the paint. In this connection it is of interest to cite the tests of Olsen and Ratner* upon the drying of linseed oil. They record a gain in weight of 18 per cent at the end of approximately 10 weeks. They also showed the elimination of approximately 5 per cent of carbon dioxide and 15 per cent of water.

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* Jour. Ind. & Eng. Chem., 3, 84.

Summary of Conclusions.

I. When linseed oil or similar drying oils are spread in thin layers, the absorption of oxygen which takes place is accompanied by the evolution of considerable amounts of carbon dioxide and organic substances. Carbon monoxide is also evolved in small amount.

II. Oil paints containing lead or zinc pigments do not emit volatile compounds of a metallic nature.

III. Drying paints evolve water-soluble acid substances such as formic acid, as well as acid substances which are apparently of a fatty nature. Carbon dioxide and carbon monoxide are also present in the vapors from the drying paint. The type of pigment used in the paint may directly affect the amount and character of the volatile substances produced. Basic pigments apparently stimulate the evolution of such products.

IV. Aldehydic substances are present in the vapors from drying oil paints. These substances probably have a marked bactericidal effect upon pathogenic bacteria and would thus account for the sanitary value ascribed to oil-pigment paints.

***J. S. C. I.*, 31, 937 (1912).

CHAPTER XV.

THE TOXIC AND ANTISEPTIC PROPERTIES OF PAINTS.

Later experiments by the writer determined, in a more satisfactory manner, the composition of oil vapors. The tests were made in the "scrim" room of a large linoleum factory where thousands of yards of cotton scrim are suspended in the air and repeatedly coated with linseed oil. As soon as one coat becomes dry, another flowing coat is applied, and the process is repeated for several weeks until a semi-transparent rubber-like mass of oxidized oil, ¼ inch thick, is formed on either side of the scrim. In this room was placed an open tin can containing a pint of ordinary tap water. After exposure to the vapors in the room for a week, the can was removed to the writer's laboratory and the contents examined. The odor of the water was very strong and suggestive of acrolein. A considerable quantity of suspended and precipitated red oxide of iron was observed. As the water originally contained iron, it is probable that its precipitation was due to the carbon dioxide given off by the drying oil. Analysis of the water showed the presence of appreciable quantities of formic, acetic and butyric acids. Aldehydes were also found present.

A consideration of the previously cited laboratory tests in which the writer discovered the presence of carbon monoxide in the vapors from drying oils and paints, will no doubt be of interest to medical authorities. The results will probably throw considerable light upon cases of poisoning which have been attributed to lead absorption, but which were possibly due to the effect of carbon monoxide upon the red corpuscles of the patient. Symptoms such as sallow complexion, general lassitude, emaciation and incoördination, caused by the inhalation of carbon monoxide over long periods of time, might easily be mistaken for symptoms of lead poisoning. When a painter, suffering badly from such symptoms, appears before a physician and informs him of the character of his work, the physician is very apt at first to diagnose the case as suspiciously like plumbism. Unless further examination be made, treatment for plumbism might be resorted to.

That great credence has been placed in the theory that white lead paint gives forth poisonous metallic vapors, is shown in the following citations from an article written by one of the most prominent medical men of the age:

> There is still considerable difference of opinion as to what takes place when men and animals who have breathed the emanations given from a surface freshly painted with white lead suffer in consequence. In my book, Diseases of Occupations,* I draw attention to the fact that during the preparation and mixing of paints, peculiar symptoms are occasionally complained of by the men, which are not altogether due to the white lead present, but to some peculiar condition of the linseed oil. Prof. Baly, of Liverpool, on spectroscopic examination of a beam ot light passed through the emanations given off by a freshly lead-painted surface, was at first disposed to regard the harmful character of these exhalations as due to lead, but further experiments convinced him that, as similar emanations are given off by linseed oil mixed with manganese dioxide, they are due to unsaturated aldehydes, arising from hydrolysis of the linseed oil. These emanations are given off more readily from surfaces painted with white lead than where zinc white has been used. They vary with the percentage of linseed oil and they are given off in descending proportions according to whether white lead, sulphate of lead, or zinc white has been the compound added to the oil. Baly is therefore disposed to regard the aldehydes evolved from freshly painted surfaces as the harmful agent and not the lead. This, however, can only be partly true. That lead emanations are also given off is more than a probability, for only thus, among other reasons, can I explain the occurrence of severe colic, anæmia, a blue line on the gums, and the presence of a small quantity of lead in the urine of a previously healthy young medical man recently under my care, who became seriously ill through living and sleeping at home when all his rooms were being painted. Besides, the experiments of MM. Heim and Hebet show that lead is present in the vapor given off from painted surfaces, and that to this circumstance the plumbism of house and coach painters is due.
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> (Excerpt from "Industrial Lead Poisoning and Some of the Problems it Raises," Sir Thos. Oliver, M. A., M. D., LL.D., D. Sc., F. R. C. P., Newcastle-upon-Tyne. Trans. XV. Internat. Congr. Hygiene and Demog., Vol. III, 826.)

At one time the present writer was disposed to place full confidence in the theory that lead paints evolve metallic vapors. His experiments have, however, afforded sufficient data to dispose of such a theory. Lead is not a metal which forms easily volatile compounds. Arsenic and antimony are the only metals which afford vapors at ordinary temperatures, the hydrides of these metals being well known and of a very poisonous nature. Antimony is often present in pig lead, and it is quite possible that the lead used in corroding the pigment for Baly's tests contained traces of antimony. If so, it is possible that sufficient vapors were produced from this lead to account for the extremely delicate spectroscopic tests which were reported, providing the results obtained were really due to metallic vapors.

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*Diseases of Occupation. Methuen & Co., London.

It is apparent that many other cases of lead poisoning have, without justice, been attributed to the vapors from white lead paints. The writer once heard of a case of lead poisoning, in which the patient (a woman) had contracted the disease while boiling out some old white lead paint pots which had been left by a painter. The patient, who was of an extraordinary robust nature, lost weight, became sallow in appearance, and developed a well-marked lead line on her gums. She, of course, attributed the poisoning to the breathing of lead fumes from the paint pots. It is probable, however, that she scraped the interior of the pots to clean them, and in so doing had collected considerable lead under her nails and in the pores of her skin. Possible failure to clean her hands properly before eating would account for the effects which followed. It is also possible that she possessed an idiosyncrasy to lead, which made the cutaneous absorption of a small quantity sufficient to cause poisoning.

A case of lead poisoning has been referred to by Klein* in citing a discussion of Baly's paper, where a young lady, the daughter of a physician, became seriously ill. A marked change was noted in her blood corpuscles. Her father had attended many lead workers and had observed a similar change in their blood when they became poisoned with lead. It was later ascertained that the young lady had occupied a room freshly painted with white lead. The father probably attributed his daughter's illness to the absorption of lead fumes from the drying paint. Klein, however, points out that the change noted in the blood corpuscles was probably due to the breathing of turpentine fumes emitted by the paint, and he describes a very simple test which he thinks might give relative results in determining the effect of various drying substances upon the blood corpuscles. He utilizes the leaf of the Japanese laurel, which turns black when placed in contact with the vapors of turpentine, benzine or similar solvents.

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* Behavior of Paints under the Conditions of Practice. Armstrong & Klein, J. S. C. I. No. 7, Vol. XXXII, April, 1913.

The present writer is convinced that the change in the blood corpuscles of a person who has breathed the fumes of drying paint in an unventilated room, is more likely due to the effect of the carbon monoxide evolved by the paint. The use of turpentine doubtless stimulates the oil present to give off larger quantities of such gas, but the effect of turpentine should be cited as a contributory effect in this respect.

Carbon monoxide, if present in appreciable percentage, is really the most poisonous constituent of the vapor from drying paint. The physiological effect of this gas is ably set forth in Bartley's Medical Chemistry, page 193, as follows:

> "*Physiological Effect of Carbon Monoxide.*—It has the power of combining with the hemoglobin of the blood and of expelling the oxygen. It thus acts as a narcotic poison; causing dizziness, headache, nausea, incoördination of movements, convulsions, and death. If the carbon monoxide be in sufficient quantity to saturate all the hemoglobin, recovery seldom takes place. The blood has a light red color and does not coagulate after death, or decompose as readily as normal blood. * * * If the hemoglobin is only partially saturated, recovery may take place, but very slowly, debility, anonxia, etc., remaining for days. Air containing 0.5% kills birds in three minutes; 2.0% renders a guinea pig insensible in two minutes. Artificial respiration is of little use. Transfusion of blood or intravenous injection of sterilized salt solution, 0.7%, is the most promising treatment. The sources of danger are open fires, defective draft in chimneys, escape of coal gas and especially 'watergas' from defective fittings or from leaks under the ground. When the ground is frozen and the gas escapes into the soil near a dwelling, the gas diffuses through the ground into the cellar, and, as it is thus deprived of its odor, persons may be poisoned and not know where it comes from. Illuminating-gas poisoning is essentially a poisoning by the carbon monoxide which it contains. Suffocation is not very different from suffocation by other gases, and should be distinguished from poisoning."

In a paper bearing upon the hygiene of the iron and steel industry, Darlington* points out the danger to workmen breathing carbon monoxide produced in "salamander" grates, as follows:

> "The chief danger to workmen is from the inhalation of carbon monoxide. When we breathe, a certain quantity of oxygen is taken into the lungs, passes into the blood and is carried by the red material of the blood to the various tissues of the body, where it is used for the production of heat and energy. The red material of the blood here gives up its oxygen, and the blood takes up carbon dioxide and carries this to the lungs from which it is exhaled.
>
> "Carbon monoxide has a greater affinity for the red material in the blood than has oxygen, making a more stable combination. The deleterious effect of carbon monoxide is due to this stability of combination with the red material in the blood, which reduces its oxygen-carrying power. Except in closed rooms, there is no immediate marked effect upon the workman, because gases diffuse rapidly in the atmosphere. But the frequent breathing of even a small amount of the carbon monoxide will in time produce anæmia. This statement is not made upon actual experiment, but on clinical experience. If the air contains more than one per cent. of carbon monoxide, it may prove quickly fatal."

The master painter may be relieved to learn from these references that paint is not the only source of carbon monoxide. Nevertheless, he will probably be impressed with the poisonous nature of this gas. It is quite certain that the amount of such gases evolved by a drying paint is insufficient to act fatally, but the painter should remember that the development of such gases is always accompanied by the absorption of oxygen from the air by the drying oil. Atmospheres are thus devitalized and rendered less capable of supporting life. A very interesting calculation may be made to show the effect of a drying paint upon the atmosphere of a closed room. The figures which are recorded below are made upon the assumption that the paint used will dry perfectly at the end of forty-eight hours.

In a living room twenty feet square and ten feet high, there is approximately 1200 square feet of wall and ceiling area, and the air content of the room is approximately 4000 cubic feet. Air weighs 36.5 grams per cubic foot, and contains approximately the following constituents:

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*The Heating of Iron and Steel Plants. Thos. Darlington, M. D. Vol. I, No. II, Bull. Amer. Iron and Steel Institute, p. 323.

Nitrogen	78.49%
Oxygen	20.63%
Water	.84%
Carbon Dioxide	.04%

The actual amount of oxygen present in the air of such a room would therefore be 30,000 grams (approximately 66 lbs.) To cover the walls and ceilings of the room, there would be required three gallons of paint which would spread at the rate of four hundred square feet per gallon. Paints weigh approximately 15 lbs. to the gallon, and contain, on an average, 66 2/3% of pigment and 33 1/3% of oil. The 3 gallons of applied paint would therefore contain approximately 15 lbs. of oil. If this oil takes the theoretical amount of oxygen required for proper drying, namely, 15% of its weight, there will be absorbed 2¼ lbs. of the 66 lbs. of oxygen present in the air. Incidentally, the linseed oil may have evolved 2¼ lbs. of water and ¾ lb. of carbon dioxide as well as smaller percentages of carbon monoxide, aldehydes, fatty or aromatic acids, etc. The air content of the room, therefore, would probably show on analysis the following:

Nitrogen	78.31%
Oxygen	19.89%
Water	1.53%
Carbon Dioxide	.27%
	100.00%

A very simple preventive for such conditions as have been pointed forth in the above discussion, may be had by supplying ventilation to a room during painting. Painters working in well-ventilated rooms have probably never suffered discomfort from the vapors of oil paints of any type. Foremen should therefore always insist upon proper ventilation whenever painters are at work.

One of the most important features connected with the formation of vapors by drying paints, is that which relates to the germicidal properties of such vapors. Foreign investigators have shown that the vapors from oil paints are very active in retarding and preventing the growth of bacteria. Tests made by the writer have also shown the marked antiseptic properties of paints.* Some tests conducted early in 1914 by the writer have shown that the vapors from oil paints are extremely energetic in destroying bacilli. These tests were made in the following manner:

Three small porcelain crucible covers were sterilized at 120° C. in an autoclave. They were then filled with sterile melted lactose agar, and the agar allowed to solidify. The agar in each cover was subsequently cross-streaked with a platinum needle, previously dipped in a culture of B. Coli Communis (of the Colon Typhoid group). The covers were then suspended by wire from the center of stoppers inserted into large glass tumblers. All of the apparatus was first sterilized before using. The first tumbler was left empty, as a blank test. Into the second tumbler was placed 3 c. c. of 40% formaldehyde solution. Into the third tumbler was placed a half ounce of oil paint. This tumbler was revolved in order to distribute the paint over the interior surface and sides. The three sets of apparatus were placed in an incubator at 37° C. and allowed to remain there for 24 hours. When removed, the agar cultures were examined and photographed. In the blank test (Tumbler No. 1), a marked growth of bacilli was shown on the surface of the agar where it was inoculated by the needle. The agar in Tumbler No. 2 showed no development of bacilli. The fumes of the formaldehyde, on account of their antiseptic action, had prevented the growth of the coli. The agar in Tumbler No. 3 also showed no distinct growth of bacilli. The fumes of the drying paint had acted apparently with almost as much vigor as the formaldehyde.

The writer is therefore fully convinced from these tests that the most efficient means of destroying bacteria in quarters previously occupied by persons suffering from contagious disease, is to be had by painting the rooms with an oil-pigment paint. During the painting, the rooms should be well ventilated, but immediately afterward they may be closed for a day or so, in order to allow the fumes from the paint a thorough opportunity for asserting their antiseptic effect upon every portion of the walls, interior and contents of the room. Fumigation with burning sulphur or washing the old paint with liquid antiseptics are probably no more efficient from a sanitary consideration, and assuredly less productive of pleasing results from a decorative standpoint than the application of a fresh coat of paint to the walls and trim of a room. Flat wall paints made of non-poisonous lithopone and zinc pigments, on account of the ease with which they may be applied, their low cost and their ability to hide surfaces with few coats, make them especially fitted for this purpose.

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* "The Sanitary Value of Wall Paints," by Henry A. Gardner. Bull. No. 2, The Institute of Industrial Research.

Cause and Prevention of Toxic Effect of Pigments.

Much has been published regarding lead poisoning, and the subject has been discussed at length both here and abroad. There can be no doubt that painters have suffered to some extent from this disease, but recorded evidence shows that the majority of cases have occurred in factories where lead products are made. A historical review of the subject will show that the hand mixing of dry lead pigments is fraught with danger. It is apparent, however, that the painter who handles prepared-paint products does not come in contact with lead dust, and his trade is therefore a safe one, free from the dangers that attend the older methods and materials.

Eminent authorities have pointed out that the inhalation of dry dust containing metallic particles floating about, constitutes the most dangerous source of lead poisoning; respiratory absorption being readily accomplished under such conditions. This, of course, calls for the elimination of dust as far as possible in the painting trade. The dangers from cutaneous absorption or from gastro-intestinal absorption, which are in most cases caused through uncleanliness of hands or face, will, of course, be reduced when more cleanly and sanitary conditions are provided, and when the rules of hygiene are more strictly observed.

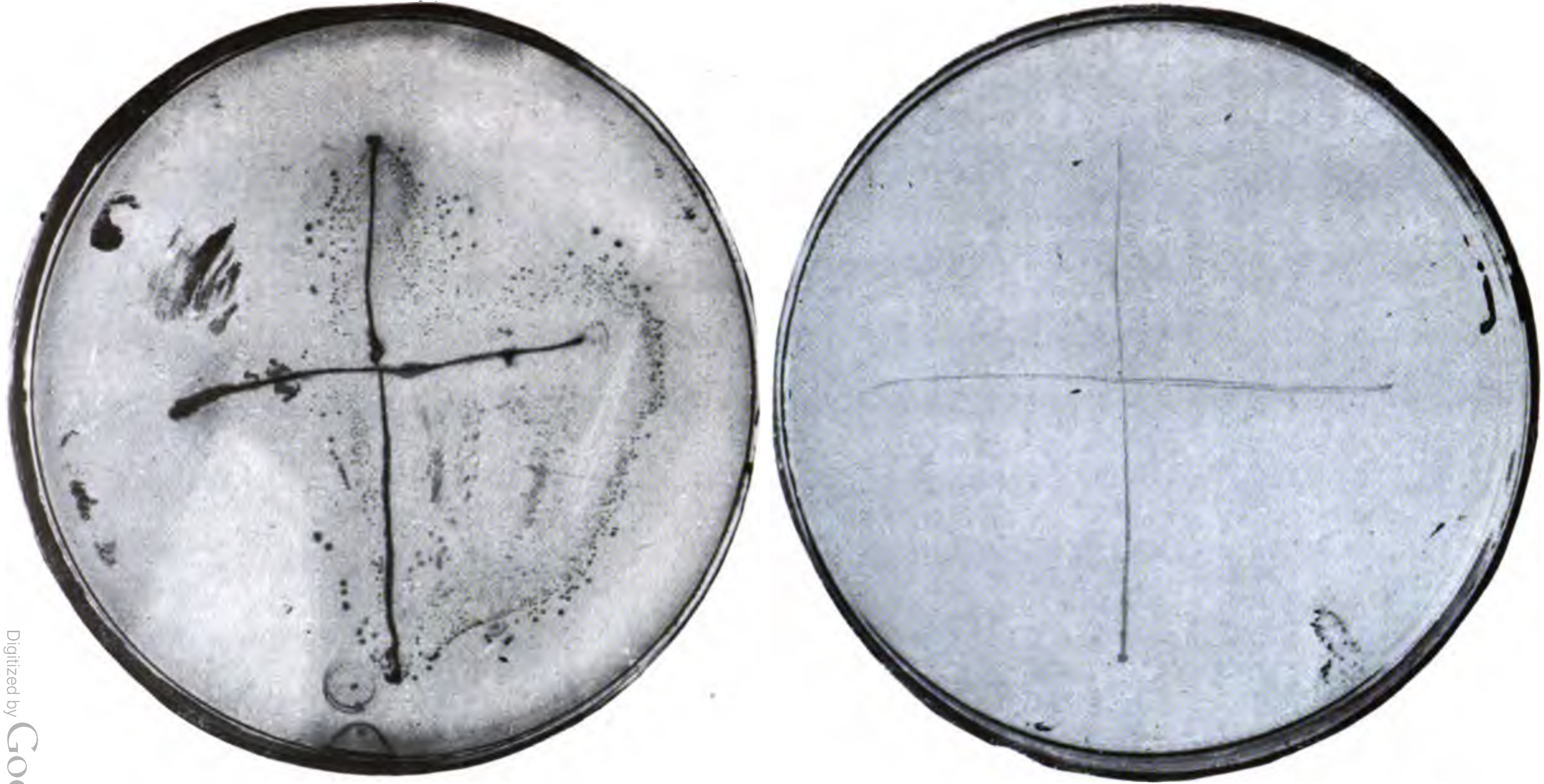

FIG. 111.

Photograph illustrating antiseptic properties of oil-paint vapors. Glass plates containing agar jelly were cross-streaked with a germ on the right was placed in a freshly painted room over night.—Note an unpainted room over night. Note growth of bacilli. The plate culture (Colon typhoid group). The plate on the left was placed in absence of bacilli growth.

The susceptibility of certain persons to metallic poisons should make such persons exert extreme care in handling lead pigments, while the same precaution should not be neglected by those workmen who are supposed to exhibit a great degree of resistance or tolerance to metallic poisons. In the latter class, the resistance to lead may be due to its elimination from the system in sufficient quantity to equalize the amount daily absorbed. It has been observed by medical authorities that workers in lead, who are thus constituted, often feel that they are free from the effect of lead, whereas, as a matter of fact, their systems may contain a considerable amount of the metal, which upon the first provocation, induced possibly by over-indulgence in alcohol, may become active and cause fatal results.

Some danger from lead poisoning may attend the removal of old lead paints. Upon battleships it is customary to use for this purpose, wide steel chisels driven by compressed air. Piled up coatings ¼ inch in thickness are easily and rapidly removed by this method. There is formed during the operation, a considerable amount of dust containing a large percentage of white and red lead. The workers are, however, only allowed to carry on such work for short periods of time. During the interim, they are placed at less dangerous tasks. In this connection it may be of interest to cite the fact that red lead as a primer for steel ships is being replaced to a great extent by sublimed blue lead, which, on account of its less poisonous nature and highly rust inhibitive properties, is to be highly recommended for the purpose.

Differences of opinion have been expressed regarding the danger of removing paint from an old painted surface by means of a torch. This method is not used at the present time, to such an extent as formerly, on account of the efficiency of liquid removers. The old torch process, however, is more economical and therefore necessary in some instances. The strong heat of the torch and the presence of dried oil and other organic substances will cause lead paints to be partially reduced as metallic lead. The temperature, however, is not as a rule sufficiently high to cause the formation of metallic vapors of lead. If the paint is made of zinc oxide or lithopone (this is not always possible or practical) there is much less danger, for these pigments are not materially affected by the heat of a torch. Moreover, zinc vapors are not nearly as poisonous as lead vapors. The truth of this statement is shown by the following excerpts from articles relating to the toxicity of zinc compounds:

> "Of 65 cases of zinc-poisoning collected by Witthause, 46 were in Great Britain and only 3 in the United States. All were caused by two salts, the sulphate and the chlorid. The sulphate was to blame in 25 cases, of which 8 were due to mistaking it for 'Epsom Salt.'"
>
> Text-Book of Legal Medicine and Toxicology. Peterson & Haines, Vol. II, p. 443.
>
> "The poisonous action of zinc oxide is so weak that it is almost doubtful whether it should be considered a poison. Dr. Marcett has given a pound (453.6 grams) during a month in divided doses without injury to a patient afflicted with epilepsy; and the workmen in zinc manufactories cover themselves from head to foot with the dust without very apparent bad effects. It is not, however, always inocuous, for Popoff has recorded it as the cause of headache, pain in the head, cramps in the calves of the legs, nausea, vomiting, and diarrhœa; and he also obtained zinc from the urine of those suffering in this manner.* Again, a pharmacy student filled a laboratory with oxide of zinc vapor, and suffered from well-marked and even serious poisonous symptoms, consisting of pain in the head, vomiting and a short fever."
>
> Poisons: Their Effect and Detection. A. Winter Blyth, pp. 689 and 691.
>
> "Brass founders' ague may be defined as an acute malaria-like syndrome of chill, fever (sometimes), and sweat, appearing a few hours after the inhalation for a few minutes or longer, of the vapors or fumes arising from molten brass or from the fumes of pure zinc alone† affecting only or mostly those unaccustomed to such exposure."
>
> Excerpts from "Occupational Brass Poisoning: Brass Founders' Ague." Dr. Emery R. Hayhurst, Chicago, Ill. Trans. Internat. Cong. Hygiene and Demog., Vol. III, 766 and 767.
>
> "In many cases large doses of the salt (zinc sulphate) have been administered for days without any symptom of toxic effects. In one instance 36 grains of salt were given three times a day for six weeks without the appearance of any symptoms of poisoning. All writers on toxicology, however, agree that in certain quantities zinc salts exercise a poisonous effect."
>
> Page 33, "Zinc in Evaporated Apples," by Harvey Wiley. Bulletin No. 48, Division of Chemistry, U. S. Dept. of Agriculture, 1896.

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* The so-called "zinc fever" has only been noticed in the founding of brass; it is always preceded by well marked shivering, the other symptoms being similar to those described.

† Lehmann, K. B.: Giess—oder Zinciieber, Arch. f. Hygiene, 1910, Bd. LXXII, s. 358-381.

A method* has been proposed for the removal of lead from the system by means of an electrical bath, the legs of the patient being partially immersed in a dilute electrolyte, which, on the passage of the proper amount of current, would remove the metallic poison from the system. Although such methods may prove of great value in the treatment of lead poisoning, it is much better for lead workers to use preventive measures which will guarantee their safety from lead.

It is pleasing to note that corroders are already alive to the value of preventive measures, and the factories of the country are all adopting safety appliances and devices which are of great merit for this purpose. The resident surgeon of a large white lead works states:

> "Dust is the curse of the lead industry, for its minute particles are surrounded by a layer of moisture which renders them more liable to absorption by the respiratory mucous membrane, so it is essential that dust in the various processes of manufacture be eliminated. Every effort has been made to accomplish this all-important factor. Our chasers are enclosed in heavy cast-iron dust-proof covers from which leads a flue with a powerful suction of air which carries all dust to one of the main organ-pipe dust collectors.
>
> "Dry sweeping is not allowed, and the rooms are gone over each day with a vacuum cleaner, which thoroughly cleans them without the creation of any poisonous dust to contaminate the atmosphere."†

The above citation indicates the great care which is exercised to prevent the absorption of lead dust in factories. Should we not exercise similar care in guarding against lead dust in our public buildings? Many tons of corroded white lead flatted with turpentine were at one time applied to the walls and ceilings of school rooms and hospitals. Gradual disintegration of such paint would result in the formation of dried particles of white lead dust. The presence of such dust in the atmosphere of a room is very dangerous to the health of the inmates. Fortunately the use of flatted white lead has been largely abandoned for wall and ceiling decoration, and its place has been taken by the more sanitary leadless flat wall paints.

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*The Decorator, Nov. 22, 1913, Vol. XII, No. 138, p. 201.

† "Safety and Sanitation in the Manufacture of Paints." Dr. Francis D. Patterson. Paint and Varnish Record, Dec. 15, 1913.

It is evident from a consideration of the foregoing discussion that with the adoption of preventive measures, the installation of dust-retarding apparatus and the wider use of prepared paint products, lead poisoning will be done away with almost entirely.

The Relative Toxicity of Volatile Thinners

The Relative Toxicity of Volatile Thinners.—The toxic properties of certain volatile paint thinners has been discussed in a most excellent treatise which has recently appeared under the title: "The Hygiene of the Painters' Trade." This publication was issued as Bulletin 120 of the United States Department of Labor. A brief digest of this article is herewith presented:

> The painting trade is responsible for many cases of lead poisoning. The use of white lead, however, is necessary in the better types of exterior paints. For interior painting, white lead may be entirely replaced by the non-poisonous, leadless paints (lithopone and zinc paints). Any type of paint, whether made of lead, lithopone or zinc, may, if thinned with large quantities of benzine, cause sickness among painters, if such paints are used in rooms where there is no ventilation. The vapors from paint products containing benzol, wood alcohol, turpentine, etc., are very injurious, some investigators having reported fatal results attending the inhalation of such fumes. The danger from this source is apparently easier to avoid than the danger attending the use of white lead. Among the various pigments used in the manufacture of paint, corroded white lead (Dutch or Carter process) is the most poisonous on account of the greater solubility of lead carbonate in the gastric juice. Physiological experiments at the University of Chicago and practical tests at the Pullman Company shops indicate that the basic sulphate of lead (sublimed white lead) is less poisonous than basic carbonate of lead (corroded white lead). The dangers attending the use of red lead as a metal paint are becoming lessened on account of the displacement of red lead by other less poisonous pigments, such as iron oxides, chromatized pigments, etc. The rubbing, sanding or burning of old surfaces painted with white lead is the cause of much of the lead poisoning. Wet methods of sanding will, if adopted, prevent the formation of lead dust, and thus reduce the danger of lead poisoning. Painters who fail to cleanse their hands properly before eating, either on account of their ignorance of the principles of hygiene, or because of lack of time and facilities for such ablutions, are apt to become sufferers from lead poisoning. Much of the poisoning in the painters' trade will disappear when certain regulations are adopted, which will provide for more cleanly and sanitary conditions.

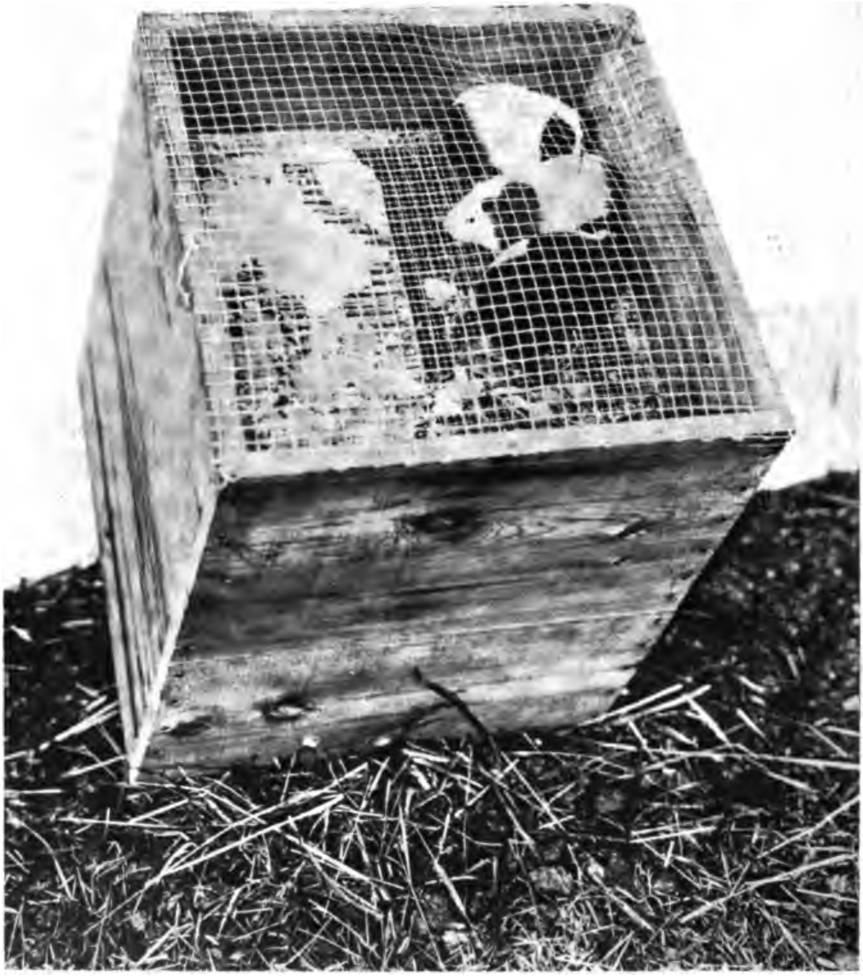

FIG. 112.

Box used for physiological test of effect of drying paint. Lower portion of box was painted on the inside. Guinea-pigs confined in upper portion immediately after application of paint and subjected to vapors from drying paint.

It is evident from the above able presentation of this subject that the thinners used in paints are in some cases quite as much to blame for the indisposition of painters as the pigments present.

The writer has for some time studied the character and physiological effect of various volatile thinners and the results of a recent series of tests are presented herewith. The tests were made by subjecting guinea pigs to the vapors of paint products, thinned with large percentages of volatile substances. The animals which were separately placed in specially designed boxes and kept under observation for a long period before subjecting them to the tests, were confined in the upper part of the boxes upon wire netting over a portion of which was placed perforated cardboard. Bedding, food and water were supplied, and the animals' weights recorded daily. The lower portion of the box was painted on the inside, the painted area averaging 16 sq. ft. and requiring for each coat about 6 ounces of paint. The paint used was white lead paste containing 10% of linseed oil, thinned in each instance with 40% of volatile thinner, such as turpentine, benzol, benzine and high-boiling point petroleum spirits.* One of the boxes was coated with shellac cut with wood alcohol (4 lbs. to the gallon). Another box was coated with shellac cut with denatured alcohol (4 lbs. to the gallon).

Subsequently, tests were made by exposing in the lower part of the boxes large open vessels containing a pint of the various thinners. The experiments were made with both ventilated and unventilated boxes. The results of the tests are shown in the following charts:

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* Now referred to in paint specifications as "mineral spirits." It is a water-white petroleum distillate having a flash point (open cup) of approximately 100° F. and 98% will usually distill between 265° and 470° F.

TABLE 18.

Experiments Conducted in Well-ventilated Boxes.

Lower compartments painted with products containing 40% volatile liquids.

Pig No.	Volatile in Paint	Weight of Animal 1st day	Weight of Animal 3rd day	Condition of Animal at end of experiment
1	Wood Alcohol	Grams 302	Grams 312	Normal
2	Denatured Grain Alcohol	291	305	"
3	Turpentine	188	199	"
4	Benzol	278	289	"
5	Benzine 68°	230	239	"
6	High Boiling Point Petroleum Spirits*	235	240	"

TABLE 19.

Experiments Conducted in Partially Ventilated Boxes.

Lower compartments painted with products containing 40% volatile liquids.

Pig No.	Volatile in Paint	Weight of Animal 1st day	Weight of Animal 3rd day	Condition of Animal at end of experiment
1	Wood Alcohol	Grams 310	Grams 308	Rather Sluggish
2	Denatured Grain Alcohol	308	305	" "
3	Turpentine	200	190	" "
4	Benzol	281	252	Dead
5	Benzine	233	233	Rather sluggish
6	High Boiling Point Petroleum Spirits	240	242	Apparently normal

*Flash Point Open Cup 102° F., Boiling Point 320° F.

TABLE 20.

Experiments Conducted in Partially Ventilated Boxes.

Open pint cans of volatile liquids placed in lower compartments.

Pig No.	Volatile	Weight 1st day	Weight 2nd day	Weight 3rd day	Weight 4th day	Condition of Animal at end of experiment
1	Wood Alcohol	Grams 298	Grams 300	Grams 293	Grams 288	Only slightly affected
2	Turpentine	201	200	196	197	Apparently only slightly affected
3	Benzol	254	255	250	241	Sluggish
4	Benzol containing 5% nitro-Benzol	302	300	290	285	Very sluggish
5	High Boiling Point Petroleum Spirits	241	239	242	240	Normal

It is quite apparent from these tests that the fumes of certain volatile liquids have considerable effect upon animals confined in quarters not properly ventilated. Rapid loss of weight is indicated in many instances. The liquid that was least volatile (high-boiling point petroleum spirits) proved least dangerous, and this result would seem to justify the opinion of many, that these spirits are most suitable as the thinners for interior wall paints.

Ordinary 62° benzine and 90° benzol, on account of their great evaporative tendencies, proved quite dangerous. The presence of nitrobenzol is evidently harmful. It caused great discomfort, from the start of the test, to the animal subjected to its fumes.

The results of Series No. 1 are interesting, for they show that when ventilation is supplied, the vapors of different volatile compounds are not effective. Such vapors are elastic substances, and they expand rapidly throughout the air in a ventilated room, their effect being dissipated by dilution. A brief description is given herewith of the various substances used in the above-described tests.

Benzol.—Benzol, a very light volatile substance, obtained as a distillate from coal tar, has been found useful as a solvent and thinner for several kinds of paint products. That benzol should be used only where ample ventilation is provided seems evident from the many cases of benzol poisoning which have been recorded.

A prominent master painter has called to the writer's attention the serious results attending the use of a well-known paint upon the walls of a cement swimming tank. The painters, while applying the first coat, suffered from severe headache and became very dizzy. The writer's analysis of the first coater used showed that it contained a large percentage of benzol. The second coater did not contain benzol. The benzol was probably used to increase the penetrating properties of the paint. The use of benzol in such a paint, upon a tank where there was no ventilation, was probably responsible for the discomfort suffered by the painters.

Glaser* comments upon several cases of benzol poisoning in Baltimore, some of which were fatal. The vapor of benzol used in the canning industry as a solvent for rubber used in sealing the cans is evidently the cause of pernicious anæmia.† Glaser thinks that the nitro-benzol present in ordinary benzol may be the active poison. If this is true, it is possible that the benzol manufacturers may be able to eliminate all traces of nitro-benzol and thus produce a benzol less poisonous in nature.

Benzol cannot very well be replaced by other thinners, for certain purposes. For instance, it is unexcelled as the thinner for exterior paints which are to be used as the primer for hard, refractory woods. In shingle stains, benzol is found most useful, as it carries the stain deeply into the shingle and provides a more enduring treatment. When thus used, upon exterior surfaces, benzol, of course, has no effect upon the painter, as its fumes are immediately diluted in the atmosphere. As a constituent of some types of asphaltic paints, benzol has found a wide use and cannot well be replaced by any other less poisonous thinner of equal solvent properties. It can, however, be used in certain bitumastic paints, in admixture with the less poisonous and less volatile thinners.

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* Report of Several Cases of Poisoning by the Vapor of Benzol. J. S. C. I., Vol. XXX, 1911, p. 519.

† Report of Dr. L. V. Selling. Johns Hopkins Bulletin, Feb., 1910.

Benzine.—Benzine, the ordinary 62° distillate from petroleum, was at one time used as a substitute for turpentine in thinning paints. When paints thus thinned were used in closed rooms, the rapidly evaporating benzine would fill the air, and cause dizziness and headache among the painters at work. An interesting example of the effect of benzine poisoning has been brought to the writer's attention. The trimming tanks and bilge boxes of a battleship were to be painted with bitumastic paints. These paints usually contain a large percentage of benzine. The compartments were difficult of access, and without ventilation except for a quantity of air that was pumped in by portable blowers. During the application of the paint, the compartment became filled with vapors which made the painters very ill. Some of the men had to stay away from work several days before recovering from the effects referred to. One of the officers of the ship went into one of the compartments during the painting, and had difficulty in returning. He became weak and dizzy and subsequently suffered from a severe headache for some time. Experiments have been made to overcome such conditions, by supplying the painters with air helmets. Such equipment is, however, unhandy, unwieldy and expensive. The use of bitumastic paints, compounded with oils and reduced only with very high-boiling point petroleum thinners,* has since eliminated the danger from such work.

The great rapidity of evaporation of ordinary light benzine when used in paints often results in the formation of pinholing, lapping, and other surface defects of an unsatisfactory nature. These conditions brought about the introduction of petroleum distillates having high flash and boiling points, similar to turpentine. These high-boiling point petroleum distillates have almost entirely replaced benzine and turpentine as the thinners for wall paints.

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* Over 100° F. Flash Point.

The use of high-boiling point petroleum thinners of this type, if properly refined, has probably never caused any discomfort to painters, especially in ventilated chambers. Through the introduction of prepared paints thinned with high-boiling point spirits, the danger which once attended "flatting work" through the use of paste paints washed with turpentine, has almost entirely disappeared.

Alcohols.—Previous to the development of denatured grain alcohol, wood alcohol was used in great quantities as the "cutter" for shellac, the high solvent properties of the wood alcohol making it very suitable for this purpose. The rapid drying of shellac varnishes to a tough, water-resistant film, developed for them many applications in the commercial world. For painting, varnishing or lacquering ships' bottoms, brew vats, floors, wooden trim, confectionery, leather, toys, etc., these products have become very useful. The fumes of wood alcohol, however, which come from the drying of shellac varnishes, may possibly be dangerous to workmen when they are confined in closed rooms or in large, unventilated vats or tanks. For this and for economical reasons, denatured grain alcohol has largely replaced wood alcohol in the varnish trade.

In a report pertaining to the chemistry, technology and pharmacology of wood alcohol, Charles Baskerville* refers to the following reported cases of poisoning from the use of this substance:

> "*Case No. 5* (193). A painter, age 39, used wood alcohol to wash varnish from hands every day after work.
>
> "Result: Became totally blind and has remained blind.
>
> "*Case No. 6* (194). A distributor of paints and alcohol in storeroom of paint factory, age 53, spilled a quart of wood alcohol on his feet and floor, and remained in same room for some hours.
>
> "Result: Became totally blind.
>
> "*Case No. 7* (195). A photographer, age 32, cleaned plates with wood alcohol.
>
> "Result: Was seized with paralysis of arms and legs, pain in sides and decrease in sight. Died after some time."

Although the cases referred to above show that wood alcohol must be handled with care, it is probable that many statements have been made regarding the poisonous nature of wood alcohol, which are not founded on absolute fact. In a pamphlet* issued by the wood alcohol manufacturers, communications are presented from large industrial concerns that are extensive users of wood alcohol. The writers of these communications apparently regard wood alcohol as non-poisonous, especially when used in ventilated rooms.

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* Wood Alcohol. Chas. Baskerville. Appendix VI to 2d Report of N. Y. State Factory Investigating Commission.

In striking contrast to this opinion, may be cited the testimony presented at the hearing held before the Ways and Means Committee of the Fifty-Ninth Congress, which shows that wood alcohol has proved highly poisonous when used in the hatters' trade as a solvent for shellac. It is probable that its constant use for long periods of time was responsible for many of the cases cited. While Baskerville points out that the danger from wood alcohol poisoning is largely eliminated when the fumes are diluted with a sufficient quantity of air, it is apparent that this precaution may not always be taken and that, under such conditions, grain alcohol would be the preferable solvent for shellac.

The following quotation from page 964 of Baskerville's article will be of special interest to master painters:

> "Local Union 111, of the Brotherhood of Painters, Decorators and Paperhangers of America, in 1905, voted that the use of wood alcohol in paints, shellac, and varnish be prohibited, and the members were warned against the use of it."

Special No. 1 Denatural Alcohol is the grade now used to some extent in place of wood alcohol as a solvent in the manufacture of shellac varnish. This special alcohol is made by mixing 100 parts by volume of grain alcohol, with 5 parts by volume of approved wood alcohol.

Turpentine.—The writer has shown† that turpentine vapors are rather dangerous when inhaled in quantity. The effect of such vapors upon the kidneys has been pointed out by Shoemaker‡ and other medical authorities.§ However, it is a matter of common knowledge that turpentine must be used as a thinner for certain types of varnishes and enamels, where a thinner of high solvent powers and slow evaporative value is required. When such products are used, therefore, it is necessary that the painter should provide ample ventilation to the room in which he works.

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* The Truth About Wood Alcohol. Wood Products Co., Buffalo, N. Y., Nov. 10, 1913.

† Paint Vapors and Their Physiological Effect upon Painters. H. A. Gardner. Presented before the M. H. P. & D. Assn., Denver, Col., February, 1913.

‡ Materia Medica and Therapeutics. J. V. Shoemaker, p. 807.

§ Peterson & Haines. Text-book of Legal Medicine and Toxicology, p. 589.

Summary of Conclusions.

Lead poisoning may occur through the inhalation of the dust from dry lead pigments, or by the careless handling and hand-mixing of lead paints. It may be prevented by establishing more cleanly and sanitary working conditions, through observance of the rules of personal hygiene and by the adoption and use of prepared paint products.

Drying oil paints do not evolve metallic vapors. They do, however, give forth small quantities of carbon monoxide gas. Paints also emit in vaporous form the volatile products used as thinners. Of these products, benzol is most dangerous, while high-boiling point petroleum spirits is least harmful. With proper ventilation, the fumes from drying paints are diluted and dissipated by the atmosphere so that they become harmless.

Drying oil paints evolve aldehydes and other germicidal substances in vaporous form. The antiseptic effect of such vapors is pronounced. The application of oil paints is therefore to be considered as one of the most efficient means of rendering living and sleeping rooms thoroughly sanitary.

CHAPTER XVI.

THE LIGHT-REFLECTING VALUES OF WHITE AND COLORED PAINTS.

In addition to toxic and antiseptic effects, interior paints should be considered from the standpoint of illumination and psychologic values. The attention of engineers is being constantly called to the relative value of different types of artificial illuminants for interior spaces. Very little thought, however, has been given to the light-reflecting power of the interior surfaces where such illuminants are used. That the surface constitutes quite as important a factor as the type of illuminant is indicated by the tests herein described, where the illumination of an interior space lighted with a tungsten lamp varied from 12 per cent. to 67 per cent. when different surface colors were used.

Athough considerable work has been done on the light-reflecting power of wall papers,* the constantly-decreasing tendency to use paper, on account of its insanitary properties, and the steadily increasing use of wall paints of the oil type, especially in hospitals† and public buildings, have necessitated a reconsideration of the problem, since different methods of determination would be required in many cases for two such different substances as paper and paint.

A search of the literature on illumination has produced one article which gives a series of carefully-made photometric measurements on the reflective value of paints. This is by Louis Bell,‡ who calls attention to the fact that traces of carbon in a paint (gray) or dust of a painted surface immensely decrease the illuminating value. He advocates the use of light-colored oil paints on account of their washability. Some of his readings are shown below. The composition of the paints is not given, and the colors are only described by terms.

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* "Surface Brightness and a New Instrument for Its Measurement," Dow and Mackinney, *Illum. Eng.*, vol. 3, Nov., 1910, p. 655. "Apparatus for Measuring Light and Illumination," Dow and Mackinney, *Elec. World*, vol. 60, Aug. 17, 1912, p. 364.

† "The Sanitary Value of Wall Paints," H. A. Gardner, Bull. Scien. Sec. Paint Mfrs.' Assn. of U. S.

‡ "Examination of the Coefficient of Different Tints in Its Relation to Indirect and Semi-indirect Lighting," Louis Bell, *Elec. World*, vol. 65, Jan., 1915, p. 211.

Color.	Kind of paint.	Per cent. reflection.
White	Oil	65.7
Extremely faint cream	Oil	64.0
Light cream	Oil	52.8
Light cream	Water	52.0
Very faint greenish	Oil	46.0
Very faint greenish	Water	45.8
Faint gray	Oil	45.6
Pale-gray buff	Water	44.0

Unfortunately, direct readings on a photometer could probably not be made with great accuracy on very dark paints or on those which present a very high enamel-like lustre. The apparent necessity of devising more appropriate means of measuring the light-reflecting powers of paint, by a method which could be used for all shades and tints, as well as all degrees of matte and gloss surfaces, led the writer to experiment with a number of types of apparatus. Painted samples for experimentation were first prepared by sizing paper and applying two coats of a number of white and colored paints of which the composition was known. The apparatus that proved most suitable for determinations of the "coefficient of reflection"* is shown in Figs. 113 and 114, as arranged by W. F. Little,† who made the readings. A disk 3¼ inches in diameter, coated with the paint in question, was placed at the centre of an integrating sphere and was illuminated by the light of a concentrated filament lamp shining through an opening in the top of the sphere. The light fell on the disk at an angle of 45 degrees. The interior of the sphere received only such light as had first been reflected by the paint. To effect a standardization a flat block of magnesium carbonate (commercial) was substituted for the disk. The value of the coefficient of reflection of this block was taken as 88 per cent., in accordance with the experiments of Nutting, Jones and

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* Defined in the 1915 Report of the Committee on Nomenclature and Standards of the Illuminating Engineering Society as "the ratio of the total luminous flux reflected by a surface to the total luminous flux incident upon it."

† Engineer in Charge of Photometry, Electrical Testing Laboratories, New York.

Elliott.* The readings were made with a portable photometer. The results are shown in the following tables and on the insert sheet which presents samples of the colored paints on paper.

TABLE 21.

Effect of the Vehicle on the Coefficient of Reflection of White Paints.

	Coefficient of reflection.
Lithopone in dark-colored raw linseed oil	61
Lithopone in very light-colored flat varnish	67
White pigment mixture in light-colored semi-gloss varnish	66
White pigment mixture in light-colored gloss varnish	66
Special white pigment in flat varnish	61.2
Special white pigment in high-gloss varnish	61.2

TABLE 22.

Effect of Slight Tints on the Coefficient of Reflection of White Pigments Ground in Flat Varnish.

	Coefficient of reflection.
Pigment A, free from impurities (very white)	66
Pigment AA, containing traces of iron giving yellow color	64
Pigment AA, tinted with ultramarine blue to correct yellow shade, producing slight greenish tint	64
Pigment A, with 1½ per cent. lampblack tinting color (light gray)	44
Pigment A, with 1 per cent. lampblack tinting color (gray)	27

TABLE 23.

Colored Paints.†

MADE ON A MIXED WHITE PIGMENT BASE, TINTED WITH CHROME YELLOW, CHROME GREEN, PRUSSIAN BLUE, PARA RED, OCHRE SIENNA, CARBON BLACK, ETC.

	Coefficient of reflection.
Light cream	66
Light pink	60
Light yellow	58
Light blue	55
Light greenish yellow	54
Light buff	52
Light green	42
Light terra-cotta	41
Medium terra-cotta	39
Light greenish blue	36
Medium blue	32
Warm green	19
Medium green	14
Red	12
Blue, dark	12
Green	11

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* "Results of Some Possible Reflecting Power Standards" in the *Transac. of the Illum. Engrg. Soc.*, vol. 9, No. 7, 1914.

† The exact color is shown on the insert sheet.

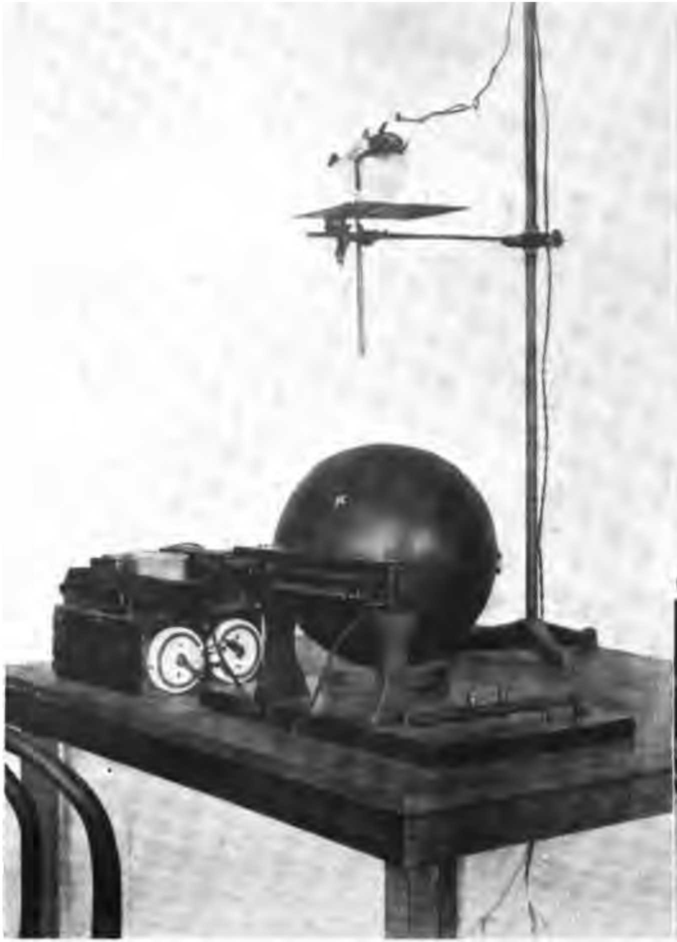

FIG. 113.
Apparatus for Determining Coefficient of Reflection of Painted Surfaces.

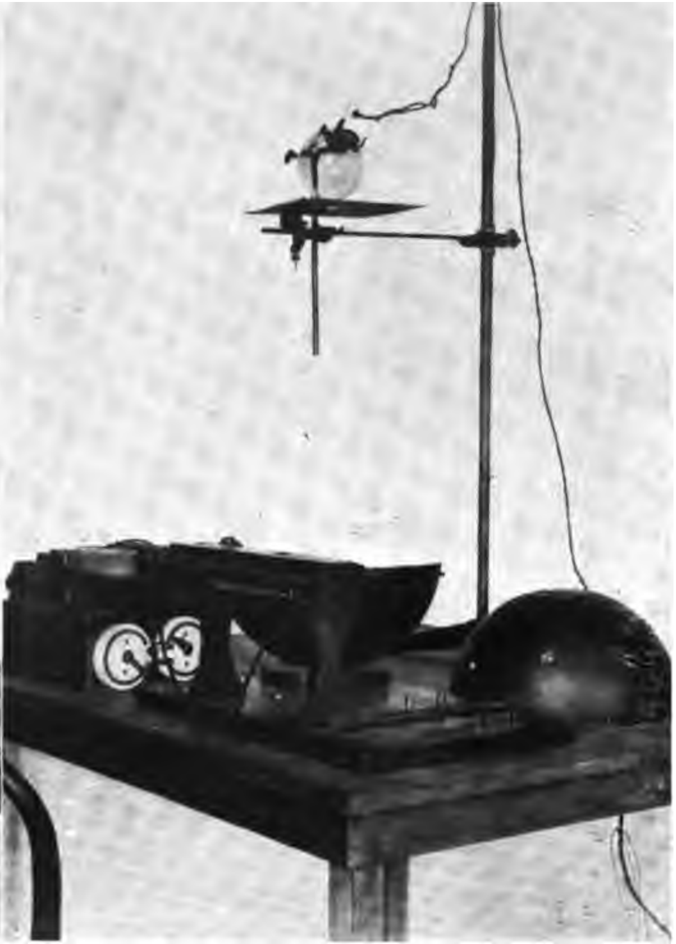

FIG. 114.
View Showing Painted Surface in Place Within Integrating Sphere.

Apparatus for Measuring Light.

TABLE 23.—Continued.

	Coefficient of reflection.
Luminous calcium sulphide paint	54.4
Aluminum paint	48.

The most interesting of the results are those on flat, semi-gloss and high-gloss paints, all of which apparently have substantially the same illuminating value when prepared of the same pigment mixture with oils or varnishes of the same degree of color. This is an important development, since it allows the use of the type of paint best suited for the lighting equipment of a room: direct, semi-indirect, indirect, etc. Although flat paints may retain their whiteness for a greater period of time, semi-gloss and gloss paints are preferred in many instances on account of their greater resistance to frequent washing.

Factory Illumination.—The illumination of factories, railroad terminals, and department stores has been given great consideration of recent years, increased output, improved workmanship, and a minimum of accidents having resulted in nearly every instance where better lighting systems have been installed. In such places, wall treatment as a means for conserving the illumination afforded by modern illuminants has generally been adopted. These advances have come as a result of practical observations which show that the rays from powerful lights, falling upon dark brick or stone walls, give less light to a room than the rays from less-powerful lights falling upon similar walls that have been painted in light colors with dust-resisting, washable paints. From the standpoint of economy it is of interest to record the fact that the monthly cost of illuminants for lighting dark-walled factories may be enormously reduced by painting the interiors in light colors.

The customary process of treating factory walls is to first apply one or two coats of flat (matte surface) white paint and lated to apply a coat of gloss white. This is the recommended treatment when the modern indirect or semi-indirect forms of lighting fixtures are used, since the gloss finish repels the lodgement of dust and may be most easily washed. For the ceilings, however, a flat or semi-gloss paint is better than a high gloss, since the former types distribute the light to better advantage. In factories where direct-lighting fixtures are used with modern illuminants, or where even less-modern forms of illumination are in evidence (swinging oil lamps, etc.), the flat or semi-gloss oil paints are also advisable, on account of their glare-preventing and light-diffusing properties.

The question has been raised as to whether colored paints should be advised for use where direct-lighting fixtures are employed, since white is not always the most desirable color under some forms of very strong light. For instance, the traveller who for the first time approaches a tropical city is surprised to see the buildings and dwellings painted blue, pink, green—in fact, every conceivable color. In Havana there exist ordinances prohibiting the use of white paints on the exterior of buildings, on account of the glaring effect produced by the tropical sun. The selection of the colors is left to the discretion of the property owner. Similarly, it is possible that in some factories paints having a slight greenish or other tint would be desirable, since a small amount of some colors may reduce the glare but will not materially reduce the illumination. The wall tint to be used should, however, be studied under the particular form of light present in a room, since artificial illumination of some types exerts a marked action upon certain colored surfaces,* giving them shades or tints which are entirely different from those observed in daylight or by other illuminants. The tint which is most pleasing under the light used, and of sufficient reflective value, should be adopted.

Schoolrooms, Public Buildings, and Dwellings.—A. C. Rapp,† of Pittsburgh, was the first to call attention to the necessity of a careful selection of colors for schoolrooms, in order to bring out the greatest mental and physical effort among the occupants. The adoption of his suggestions would doubtless result in greater efficiency in the schoolroom and a higher degree of physical fitness among the students. In his paper Rapp quotes some experiments conducted by Dr. L. E. Landon on students placed in rooms treated with various colors. The effects of the colors may be summed up as follows:

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* "A Standard for Color Values," D. McF. Moore, *Proc. Illum. Eng. Soc.*, vol. 5, 1910, p. 209. "Reflection Coefficients." P. F. Bauder, *ibid.*, vol. 6, 1911, p. 85. "Influence of Colored Surroundings on the Color of the Useful Light." *Elect. World,* 1913, vol. 61, p. 410.

† "Surfaces and Colors for Hospitals and Schools," A. C. Rapp, Bulletin 38, Scientific Section Paint Mfrs.' Assn. of U. S.

Black.—Melancholia. Decreased work.
Red.—Temporary stimulation followed by a reaction, accompanied by nervousness and headache.
Blue.—Calmness and seriousness.
Green.—Increased vitality. Happiness.
Yellow.—Increased vitality. Amiability.

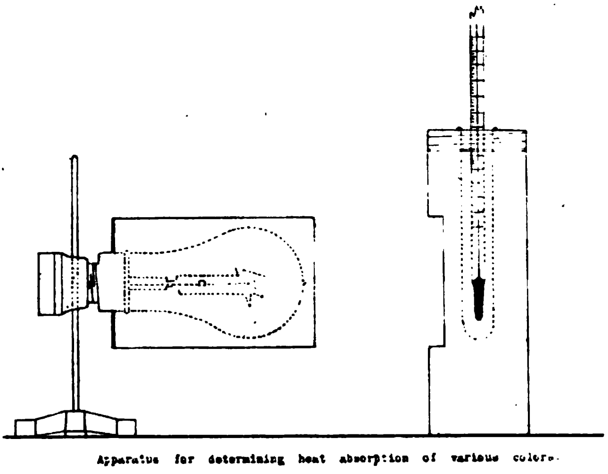
Apparatus for determining heat absorption of various colors.

FIG. 115.

Apparatus for Determining Heat Absorption of Various Colors.

That the same consideration should be given to the selection of wall colors for all public buildings, stores and dwellings, as well as schools, is apparent. It is the writer's contention, however, that the lighter tints of the most desirable colors should be used, in order to increase the illumination to the greatest possible extent. The darker colors could be used for borders and dadoes to produce pleasing contrasts to the main body of the work. These suggestions are in line with those advanced by Parsons and Smith,* who studied the physiological effect of colors in study-rooms at the United States Naval Academy. They advocated ceilings painted white, slightly tinted with yellow, and light greenish-yellow walls which by tungsten light would assume a pleasing green color.

Carriers.—Subterranean travel has increased to such great proportions in our large metropolitan centres that the problem of lighting subway cars is one of growing importance. Every paintable surface in the cars should be coated, preferably with gloss paints in white or the lightest tints. Even the floors should be painted, not with dark-gray or similar light-absorbing colors, but with neutral buff or light tints of sufficient strength to prevent them from being readily soiled. By the use of hard drying, abrasion-resisting paints for this purpose, the floors may be maintained in a sanitary condition by daily

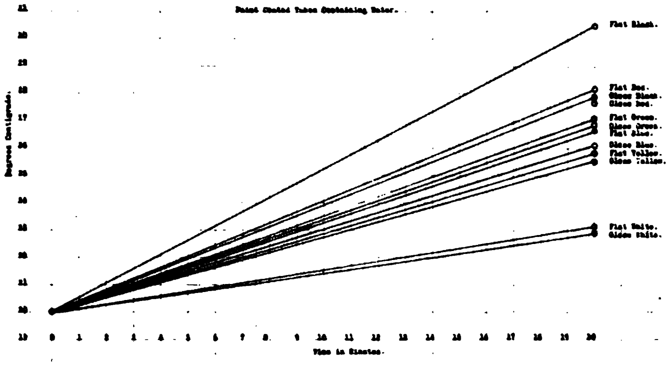

DIAGRAM III.

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* "The Illumination of Study-rooms," *Elec. Review and West Elec.*, vol. 57, Aug., 1910, p. 428.

washing. The darkest sections of tunnels may be rendered brighter by the occasional application of water-resisting white paints, where the expense of such procedure is justified. Not only in subway cars, but in surface cars and railroad passenger coaches, similar paints should be used. The present method of finishing car interiors in artificial mahogany grain could be superseded by the application of white and light-tinted paints. Reading at night without eyestrain would then be more of a possibility for the traveller.

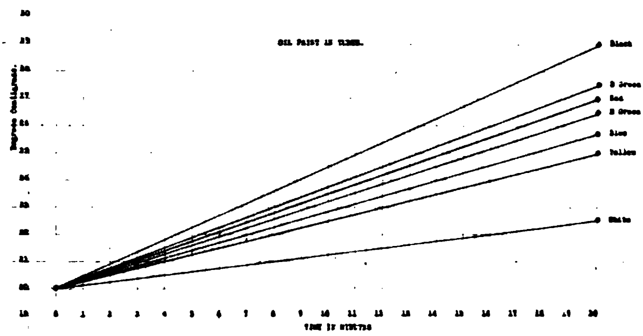

Diagram IV.

Temperature of Colored Surfaces.—Dark-colored paints not only absorb light rays, but heat rays as well. The presence of only a small amount of black in a white paint (gray) makes an astounding difference in the heat absorption. The writer and L. P. Hart have conducted some tests on those colors which are used by the grinder in producing colored paints on a white base. In one series of tests the colors were ground in linseed oil to a stiff paste which was placed in glass tubes upon which were focussed the rays of a powerful nitrogen-filled Mazda lamp (see Fig. 115). In another series of tests the outside of the tubes was painted with the same colors ground in linseed oil to produce a glossy surface or ground in turpentine to produce a flat surface, 10 c. c. of water being subsequently placed in each tube, all of which were submitted to the same light test. The rise in temperature of the paint and the water is recorded in Diagrams I and II. The colors used were as follows:

Paranitraniline red (20 per cent. on calcium carbonate base).
Chrome yellow, 100 per cent.
Prussian blue, 100 per cent.
Dark green (100 per cent. mixture of blue and yellow).
Medium green (20 per cent. dark green on barium sulphate base).
Black (100 per cent. carbon black).
White (white lead and white zinc, 50 per cent. each).

Later on in some tests made to determine the most suitable finish for oil tanks the writer found an astounding difference in the heat-reflecting properties of various colors.

This fact should be studied by the contracting painter who is called upon to paint the enormous areas presented by metal oil tanks. Such tanks may contain light distillates which, upon becoming warm, produce highly expansible vapors. When black or dark-colored paints have been used, rapid absorption of heat takes place, and considerable losses by evaporation are apt to occur. White or light-colored paint should therefore be used for the finishing coats on oil storage tanks. Paints presenting a high gloss are, moreover, less absorptive of thermal rays than those presenting a matte surface.

TABLE 24.

Rise in Temperature of Benzine Contained in Small Tanks Painted in Various Colors (Gloss Finish), When Subjected to Rays of Carbon Arc for Period of Fifteen Minutes.

Color.	Rise in Degrees Fahrenheit.
Tin Plate	19.8
Aluminum Paint	20.5
White Paint	22.5
Light Cream Paint	23.0
Light Pink Paint	23.7
Light Blue Paint	24.3
Light Gray Paint	26.3
Light Green Paint	26.6
Red Iron Oxide Paint	29.7
Dark Prussian Blue Paint	36.7
Dark Chrome Green Paint	39.9
Black Paint	54.0

Since, in the writer's experiments, white paints faintly tinted have given substantially the same heat-reflecting properties as white paints, the former should be given the preference, as they are more restful to the eye and more durable on long-time exposure. The same consideration should be observed in the painting of gas-holders.

The writer's experiments were made on a series of small cylindrical metal tanks, the exterior surfaces of which were painted in various colors. The tanks contained a standard amount of benzine. Through the pressure opening in the tops accurate thermometers were inserted. The tanks were individually placed in a cabinet containing an open front and subjected to the rays of a powerful arc light for 15 minutes. The rise in temperature of the benzine is shown in the above table.

Although plain tin, on account of its smooth, bright surface, gave the best results, it does not constitute a practical finish, as iron coated with tin corrodes on exposure unless protected with paint. Aluminum paint gave very good results, but is not nearly as serviceable as a lead and zinc linseed-oil paint.

CHAPTER XVII.

FORMATION AND INHIBITION OF MILDEW IN PAINTS.

The formation of mildew upon the surface of green paints such as are used so widely upon the exterior trim and shutters of frame builings has often been observed by the property owner. In damp localities, especially along the sea coast, the mildewing of painted exterior surfaces is not an uncommon sight, and the painter has searched in vain for materials which would prevent such conditions. A study of the subject of mildew, was undertaken by the writer when, during the course of the examination of a red lead paint which had shown a peculiar thickening action, certain types of fungi were discovered. The paint had not hardened up as is usual with pure red lead paints which are kept in containers for a considerable period, but the pigment, portion seemed to have no affinity for the oil in which it was ground, a peculiar gelatinous condition being observed. Around the edges of the paint a slight film had formed, and white spots were observed to be present upon the surface of this film. These white spots had the appearance of the type of mould that is often found upon damp basement walls. A portion of the skin was removed and preserved for microscopic examination.

There was obtained a sample of the original linseed oil in which the red lead was supposed to have been ground, and it was thought advisable to examine this oil as well as the oil floating upon the top of the partially settled pigment, to find out whether both oils were pure. The analysis of the original oil gave the following results, which indicate that it was pure linseed oil:

Color: Light amber with a distinct green fluorescence.

Iodine number	185.2
Acid number	3.4
Ash	.14%

The oil that was poured from the top of the settled red lead pigment had the following constants:

Iodine number	179.1
Acid number	8.8
Ash	2.78%

In the latter analysis the lower iodine value and higher acid number and ash presented differences which could easily be accounted for by the action of the red lead upon the oil. The analyses would therefore indicate that both samples of oil were pure. Curious to state, however, the oil that had been poured from the top of the red lead paint had an odor resembling fish oil, and the use of the latter oil might be held accountable for the condition of the paint. After standing in a bottle for forty-eight hours, the oil became very turbid and viscous, air bubbles having developed throughout the mass. Upon the surface of the oil there had formed a slight film which was covered with very small white spots. A portion of the oil was tested to determine whether there was any large amount of free glycerine present. A small amount was found, suggesting that hydrolysis had taken place. Such hydrolysis, however, might be accounted for by the action of the red lead upon the oil, wherein free fatty acid had been formed, accompanied by the splitting off of glycerine.

A more exhaustive test of the sample to determine whether fish oil was present was made according to the method outlined by Eisenschiml.* The original oil and the oil from the top of the can were separately dissolved in a mixture of chloroform and acetic acid and an excess of bromine added to each sample. The test-tubes containing these mixtures were placed in hot water for fifteen minutes. The original oil did not show any precipitated bromides; while the oil from the red lead paint showed a very large quantity. With raw oil, the precipitation of insoluble bromides would constitute a positive test that fish oil was present. It has recently been found, however, that this test is not of great value when applied to the examination of a boiled linseed oil. Inasmuch as the oil from the top of the red lead paint was shown by analysis to contain over 2 per cent. of lead ash, it might be considered

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* *Jour. Indus. and Eng. Chem.*, 1910, p. 43.

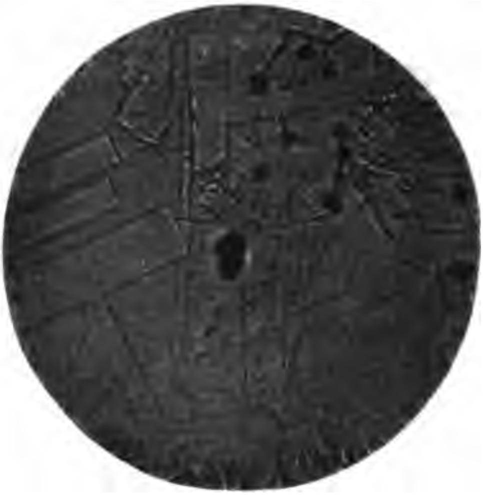

FIG. 116.

Crystals of Cholesterol Extracted from Menhaden Oil. × 750.

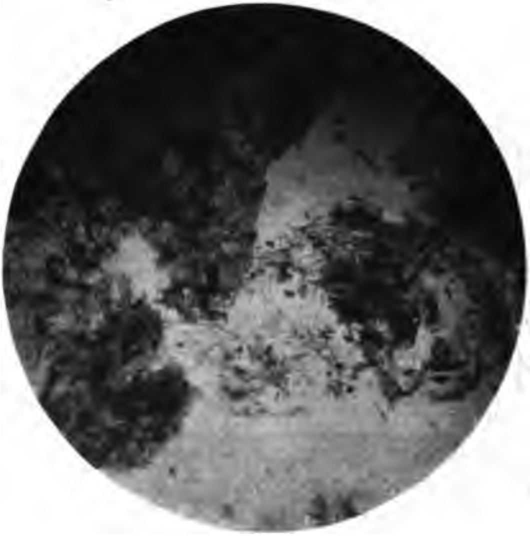

FIG. 117.

Appearance of Mould upon Dried Film of Oil. × 750.

of the same constitution as a boiled oil. Another test, however, which seemed to indicate the presence of fish oil, was made by rubbing a few drops of the oil briskly between the palms of the hands. A very rancid odor was immediately developed: This odor, however, might have been due to the presence of the free fatty acids in the oil, resulting from the hydrolyzing action of the red lead.

At this juncture in the research it was thought that considerable light might be thrown upon the work by a very careful examination to determine the unsaponifiable constituents of the oil. It is well known that in animal oils such as menhaden oil or other fish oils there is present an unsaponifiable constituent termed cholesterol, a crystalline alcholic body which is entirely absent in vegetable oils such as linseed oil. The latter oil, however, and most other vegetable oils contain a similar unsaponifiable body termed sitosterol. These two bodies are easily differentiated by microscopic examination. Portions of the oils were separately treated with alcohol, the alcoholic extract being saponified and afterwards treated with ether.* The ether extract, containing the non-saponifiable bodies, was filtered and evaporated nearly to dryness, being subsequently filtered and then taken up with alcohol. Slow crystallization of the alcoholic solution resulted in the formation of tiny crystals which were examined under the microscope. Both the original oil and the oil used in the manufacture of the red lead paint deposited crystals which when observed under the microscope seemed to be in tufts of star-like groups, probably of a monoclinic system of crystallization (pure sitosterol). These crystals did not in any way resemble the crystals which are known as cholesterol, and the above tests presented pretty conclusive proof that the oil originally used was a pure vegetable oil. A similar test, however, was made with a sample of pure menhaden oil as a blank. After the usual course of treatment, there was obtained a considerable quantity of white crystals which when observed under the microscope appeared as flat, rhombic plates which are characteristic of the crystals of cholesterol. The melting point* of the crystals from the linseed oils used in grinding the red lead paint was not determined, the writer being unable to find present any crystals which had the appearance of those found in the menhaden oil (see Fig. 116).

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* *Jour. Soc. Chem. Indus.*, 17, 954, 1898; "Chemical Technology and Analysis of Oils," etc., Lewkowitsch, vol. i, p. 470; "Oil Analysis," Gill, p. 91.

That the peculiar condition of the red lead paint, previously described, was due to the action of some type of micro-organisms seemed evident. Recourse was therefore had to the examination of what appeared to be mould upon the surface of the red lead paint previous to its chemical examination. A portion of the film upon which the mould had grown was carefully treated with ether to wash away any undried oil. After drying, the film was placed under the microscope. The appearance of the film is shown in Fig. 117. A test-tube

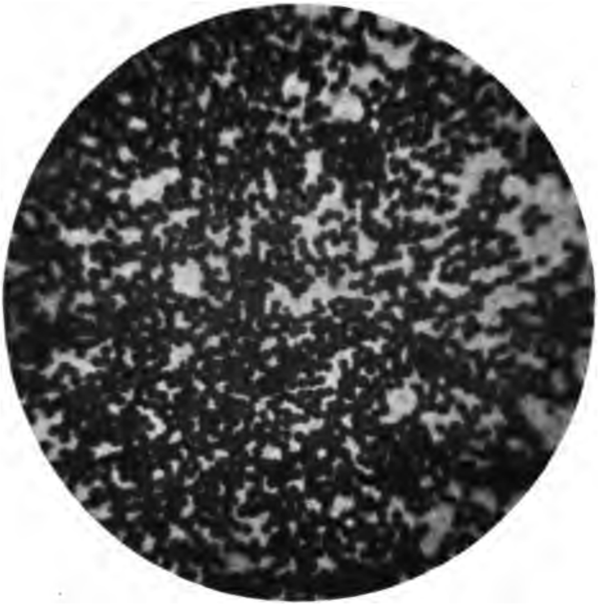

FIG. 118.

Culture of Spores from Linseed Oil. × 750.

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*Jour. Soc. Chem. Indus., 1899. 557.

culture in agar-agar was made of the mould upon the film. The surface of the agar-agar at the end of twenty-four hours was covered with a greenish mould, while there was shown to have developed downward through the jelly a peculiar white formation. Portions of both growths were examined under the microscope. The white portion was of unicellular structure, as shown in Fig. 118, while the green portion showed distinctly the mycelium with the attached cellular spores (see Fig. 119). These spores and mycelium have the distinct appearance of penicillium crustaceum. The writer is of the opinion that spores which are responsible for the mildewing of paint may exist in nearly all samples of raw linseed oil, as accidental impurities obtained from the exterior of the crushed seed.

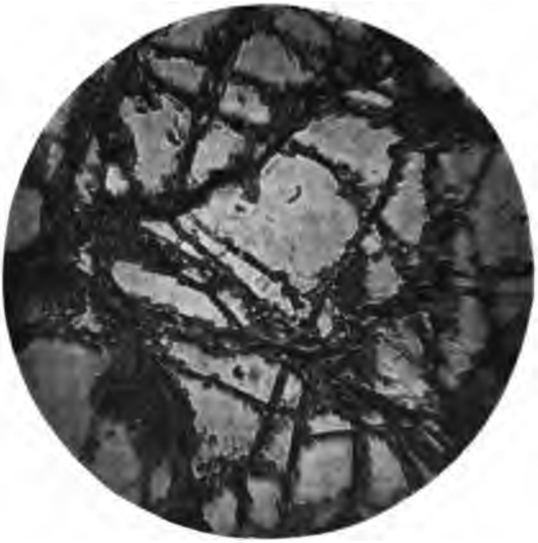

FIG. 119.

Penicillium Crustaceum Growing upon Linseed Oil Film. × 750.

The writer has previously found during the course of other experiments, conducted during the past few years, that the use of 5 per cent. of solvent naphtha or 160° benzol, added to the paint previous to application, prevents to a great extent the formation of mildew. On account of the xylol and toluol content of solvent naphtha, both of these constituents having high boiling points, they are retained in the drying film and they serve to inhibit the formation of the fungus. Another material which might serve the same purpose is refined pine oil, a water white product of very high boiling point, resulting from the distillation of turpentine. Both solvent naphtha and pine oil have excellent penetrative properties and when used in an exterior paint serve to carry the pigment into the fibres of the wood to produce a firm foundation coat.

CHAPTER XVIII.

FUNGI ON PAINTED SURFACES.

During a visit to New Orleans in the spring of 1915, the writer's attention was called to several structures, the beauty of which was marred by fungous growths referred to by the painters as mildew. The condition was not universal, but appeared to prevail upon certain types of paint. Upon such paints it was found to be most severe in the sections which were shaded by trees or in partially-sheltered nooks where dampness would be maintained for a considerable period of time. If a window shutter had remained fastened back against the side of a dwelling for a month or so, the covered surface, upon inspection, would be found several shades darker than the rest of the house, many dark mildew spots being exhibited. The under sides of veranda roofs, as well as porch columns, also suffered severely in the same respect. It was quite apparent that the paint had in such instances remained soft or become softened by the action of moisture, thus presenting a surface to which adhered insects, cobwebs, and various organic substances carried by the wind. Since many of the streets of the city contained dust which may have originally been part of canal or river bottoms, it is quite apparent that much decayed animal or vegetable matter could be entrained by soft paint, thus supplying the spores responsible for fungous growths. Structures painted for several years with yellow paint seemed especially subject to fungus. It was found that the custom at one time was to use a colonial yellow for the body of houses, this paint having been prepared from carbonate of lead, using ochre as a tinting material. Recent experiments* have shown that lead paints mixed with inert or silicious pigments never dry properly and are subject to great darkening, caused by the retention of dust particles.

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* Report of Sub-Committee X on Inspection of White Paint Test Fence at Washington, D. C., Proc. A. S. T. M., vol. xiii, part i, pp. 287-311.

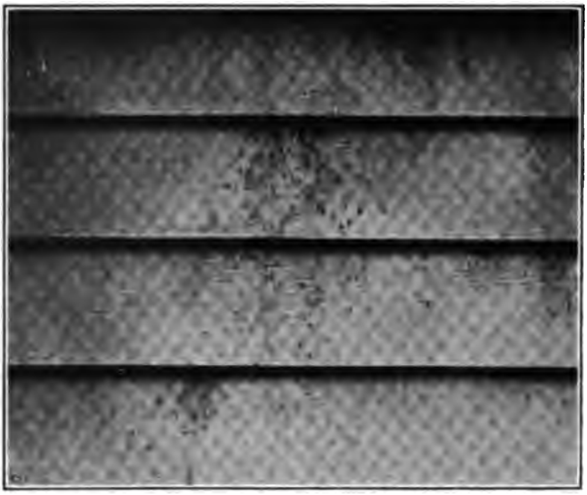


FIG. 120.
Section of Dwelling Showing Growth of "Mildew."

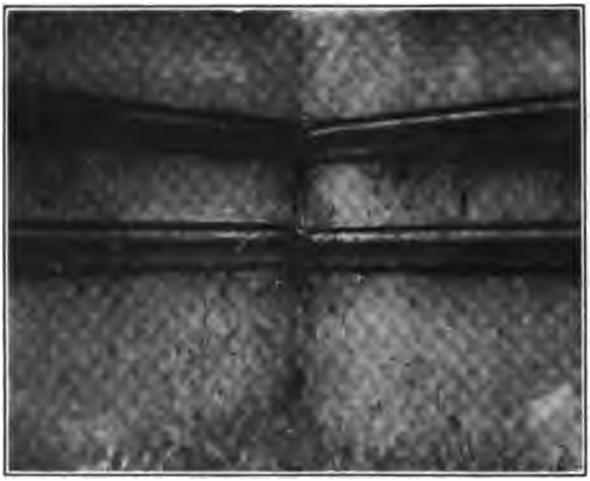
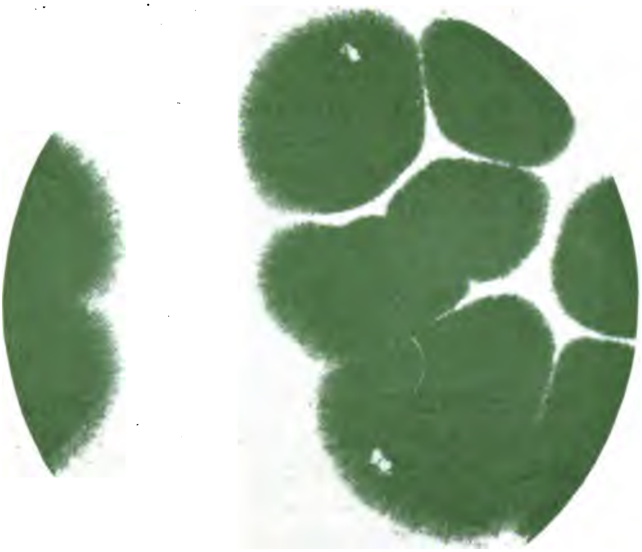


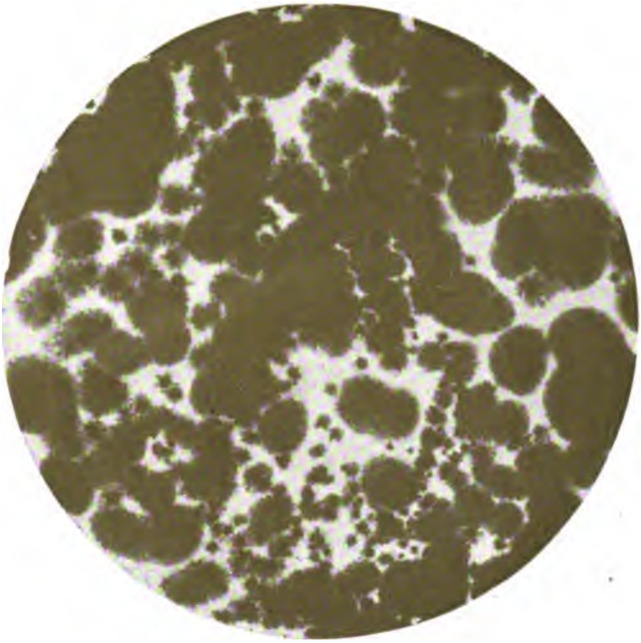
FIG. 121.
Appearance of Painted Surface Marred by Fungous Growth.

FIG. 122.



Species of green Penicillium obtained from mildew on painted surface.

Fig. 123.



Species of Penicillium (olive green). (See text.)

During the inspection trip sections of painted surfaces showing marked formation of "mildew" were collected on lead-coated structures at Hearstville Levee, Carrollton, St. Charles Avenue, Bayou St. John, and other outlying points of the city. In some instances the mildewed surfaces were lightly scraped with a clean knife, the darkened scrapings being collected in a special envelope. Small pieces of wood with the fungus intact were also removed. For the purpose of examining these specimens, it was thought advisable to prepare a culture medium which would exert an inhibitory action upon ordinary bacteria which might be present upon the specimens but which would allow the rapid propagation of the fungous spores. Since cypress is one of the most important woods used for construction purposes, especially in the South, a cypress decoction was decided upon. This was prepared in the following manner, from a section of cypress wood obtained in New Orleans: Fifty grammes of finely-divided wood shavings were boiled in a half litre of distilled water. The decoction was filtered and 1½ per cent. by weight of thread agar was added. After steaming to obtain solution, the mass was filtered, tubed, and sterilized at 120° C. for fifteen minutes.

The infected paint specimens were embedded in the melted special agar placed in Petri dishes. The spores scraped from some of the infected areas were dusted upon the surface of set agar in similar dishes. These were placed in an incubator arranged with an electric thermostat set at 37° C. At the end of periods ranging from twenty-four to ninety-six hours marked growths developed on every plate. The moulds grown in this manner were of mixed types. The various kinds of fungi were isolated, and pure cultures were grown on agar in test-tubes, subsequently plating out the different species in Petri dishes. Some of these are shown in Figs. 122 to 125. Figs. 126 to 128 show their appearance under the microscope. Since the staining of fungi is a very difficult operation, some trouble was experienced in preparing slides for examination and photomicrographic record. It is felt, however, that those shown are fairly representative of some of the various species grown.

The two principal types of fungi which were developed from the mildewed surfaces were shown to be species of Aspergillus and Penicillium. In order to determine the relative resistance of these fungi, small sections of the specimens on agar were placed on painted boards which were kept in a chamber at a temperature favorable to their growth. In this test the black Aspergillus present proved most hardy, the others seeming dormant unless kept constantly moistened. In one test the black mould in a week's period exerted a most destructive effect upon a board coated with white lead in oil. Apparently the oil served as a most favorable medium for its development, thus playing one of the leading rôles in the reactions which resulted in the destruction of the paint and

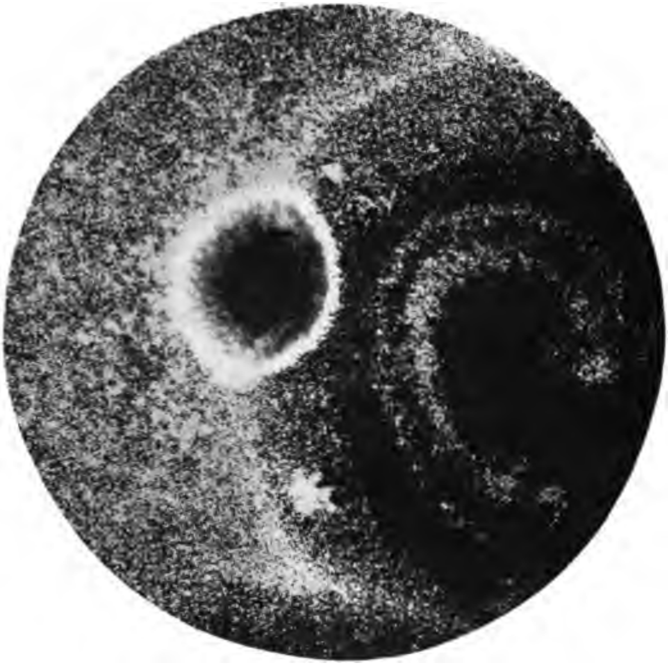
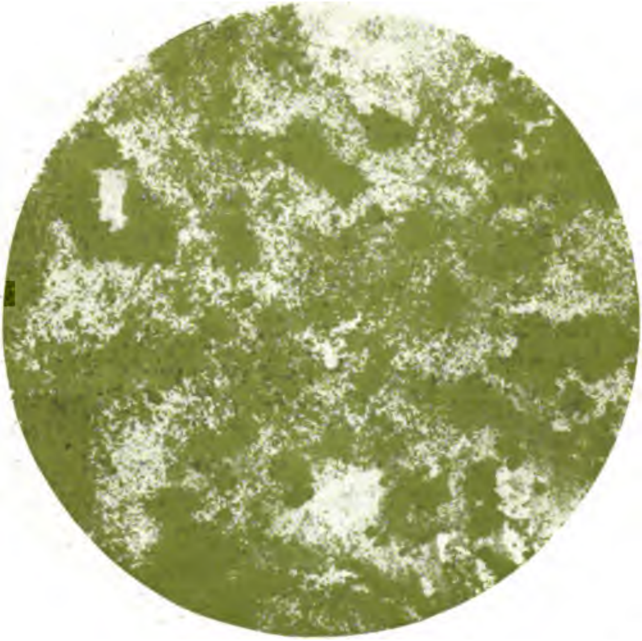


FIG. 124.

Species of Aspergillus (Black) With Spot of Penicillium (Green) in Center. The Effect of This Fungus on Painted Surfaces is Shown in Fig. 129.

FIG. 125.



Species of green Penicillium that has developed yellow pigmentation in media. (Yellow undercolor not shown in plate.)

exposure of the wood. This action is recorded in Fig. 129. The development of the fungi in every instance was much more rapid upon paint coatings which were soft and subject to retention of moisture. Paints which presented a firm, hard, moisture-shedding surface resisted the fungi and prevented germination of the spores. The board tests were then duplicated by floating the painted specimens inoculated with fungi upon the surface of water contained in a tank. The same comparative results were obtained. The paints which dried with a soft, tacky film were prepared from white lead. Those which dried to a hard, resistant film were composite paints containing white lead and zinc oxide. From twenty-five to fifty per cent. of the latter pigment was used to produce a resistant film. The oil used in all paints was linseed oil, to which was added five per cent. of liquid drier. Although it is possible that the absence of "smuts" on paints containing zinc oxide may be due to the formation in the paint film of a zinc salt which acts as a powerful fungicide, the writer is inclined to believe that the real value of the zinc is to be ascribed to its film-hardening characteristics. The addition

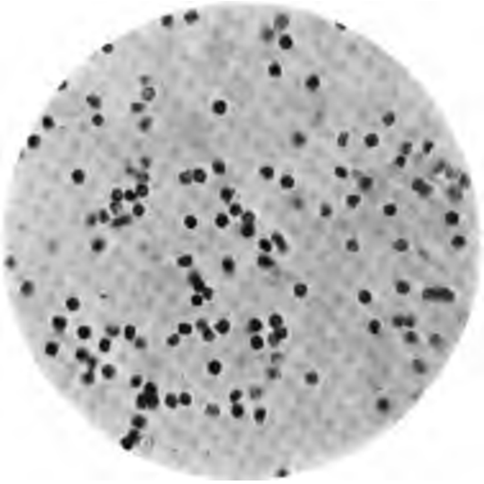


FIG. 126.

Spores of the Green Penicillium. × 1400.

of turpentine is also to be advised, since more rapid oxidation and firmer films are obtained.

It is customary for the lumber mills in some sections of the South to float the timber in adjacent ponds previous to sawing. These ponds sometimes contain dirty water filled with decayed vegetable matter and covered with colored scum. It is possible that various substances favorable to fungous growths are thus soaked up by the wood. When cut, used as siding, and painted, these substances may be leached out on some occasions. It is possible that this effect would be prevented by treating new lumber with a coat of sodium fluoride solution previous to painting. The writer's tests indicate the high fungicidal value of such treatment. It is likely, however, that the use of hard-drying, dust-resisting paints would prevent the growth of fungi which might be present on the wood used. Before leaving the subject of mildew, it is of interest to quote from the findings of G. Massee,* who records a peculiar pink-colored fungi growing on white lead paint in a conservatory:

"*A New Paint-destroying Fungus.*

(PHOMA PIGMENTIVORA, MASSEE.)"

> "Among the most remarkable of fungi is one that elects to grow on fresh paint. It flourishes in the greatest profusion in hot-houses, its development being apparently favored by a high temperature and constant humidity, as it is but rarely observed on paint elsewhere. About a month or two after a hot-house has been painted, more especially if white paint has been used, numerous small, pale rose-colored specks appear on the paint; these specks gradually increase in size and change to a purple, or sometimes dark red, color, suggesting the idea of blood having been sprinkled over the paint. In course of time the discolored areas extend considerably and form broadly-effused patches several inches across. About a week after the colored patches are fully developed, their surface becomes studded with minute, blackish-

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* Royal Botanic Gardens, Kew, Bull. of Miscel. Information, 1911, London.

red warts. Each wart is a fungous fruit, containing myriads of very minute spores, which in due course are dispersed and start new points of infection.

"When the spores of the fungus are sown on a streak of wet white paint, a faint roseate tint appears in about a week's time, and within three weeks fruit is produced in abundance, and the deep purple characteristic blotches are well developed. Spores sown on a thin smear of pure linseed oil germinate as readily as in paint, but the mycelium remains colorless, and so far, no fruit has been produced. The result is the same when the spores germinate in ordinary nutritive media or in water. No germination takes place when the spores are sown on a streak of pure white lead or carbonate of lead (pigment). Hence this substance alone is not a suitable medium for the growth of the fungus, although its presence is necessary to enable the plant to complete its normal course of development, and it is also the constituent from which the fungus produces as a by-product the purple-red coloring matter, which is collected in oily-looking drops within the cells of the mycelium, the cell-walls themselves remaining colorless. The red color suggests that the white carbonate of lead undergoes some chemical change induced by the presence of the fungus, resulting in the formation of red oxide of lead. This matter, however, requires careful investigation. The presence of two per cent. of carbolic acid in paint completely arrests the development of the fungus. The following is a technical description of the fungus:

"'Phoma pigmentivora, Massee. Maculæ suborbiculares, determinatæ, læte rosaceæ vel rosaceo-purpureæ, 1-8 cm. diametro. Perithecia in maculis laxe gregaria vel confertiuscula, vix prominula, purpureoatra, subglobosa, contextu parenchymatico, ostiolo vix papillato donata, 125-150 u diametro. Sporulæ ellipsoideæ, hyalinæ, 4-6 x 2-2.5u.'"

Washing of Paint Caused by Inferior Oil.—That microörganisms may play an important role in the behavior of materials of painting is the conclusion of the writer, based upon recent investigations into the causes of certain painting defects which have been referred to by the painter as saponification or washing. This condition is generally indicated by the appearance of a white deposit at the base of porch columns and by the paint assuming a soap-like condition if rubbed. Although the instances of such actions are rare, an apparent epidemic has recently been shown to exist in one community. The writer has made an inspection of the structures where the trouble occurred, collecting samples of the washed paints for analysis. The investigation also included the analysis and examination of the materials used in the paint, including the oil that was mixed by hand with the paste paint. Almost invariably the oil used was found to contain considerable moisture. When a bottle containing the oil was shaken, large numbers of water bubbles would appear and the oil would form a cloudy emulsion. The oil also contained a large percentage of mucilaginous or albuminous matter which is commonly called "foots." In the pressing of flaxseed, the oil is filter-pressed. This, however, takes out only a portion of the suspended matter. After standing a short period of time, certain types of albuminous matter in solution in the oil begin to precipitate out, forming flocculent precipitates which are known as "foots." Im-

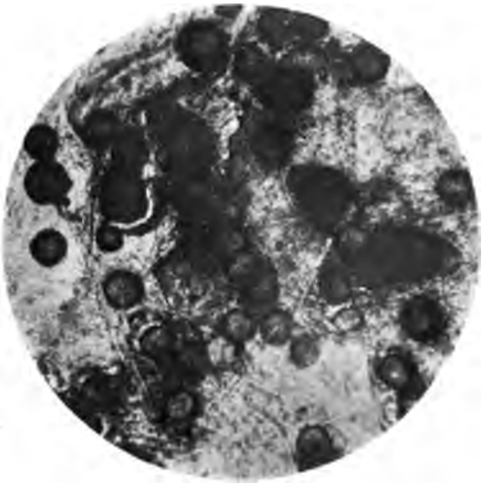


FIG. 127.

Mycelium and Sporangia of the Black Aspergillus. × 110.

properly filtered oil, that is rushed to the consumer without proper clarification, always contains such impurities. Portions of the foots from the various samples of oil collected were placed upon sterile agar, and in a few days marked growths of a peculiar pink-colored mould were obtained (see Fig. 130. This mould was identified as a species of Fusarium by V. K. Charles, Assistant Mycologist, Bureau of Plant Industry. Portions of this mould placed upon oil seemed to have a marked effect in changing the constants of the oil, free acid being produced. This result gave a clue to the causes of the washing of paint in which the infected oil was used, and indicated the nature of the intricate reactions which would be occasioned in the drying paint films. The enzymes and microörganisms in the foots apparently exert a fat-splitting action, the oil being broken up into glycerine and fatty acids, causing the formation of soap-like products which are acted upon by moisture. The glycerine formed in the film is, of course, non-drying in nature, serving to keep the paint soft and tacky, in which condition it readily attracts

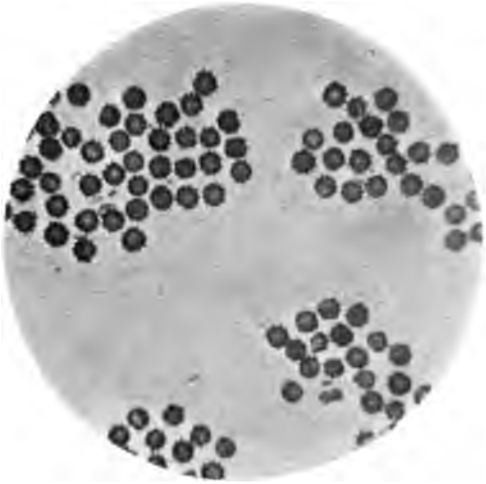


FIG. 128.

Spores of the Black Aspergillus. × 1400.

moisture from the air. The moisture thus absorbed by the film emulsifies with the soft paint, some of which washes off, depositing upon any convenient surface.

The writer has found that there is no selective action in the washing of the paints; in other words, there is no greater tendency for a lead paint to wash than a zinc paint. This was confirmed by the analysis of the washings piled up at the base of some hollow fluted porch columns at various residences.

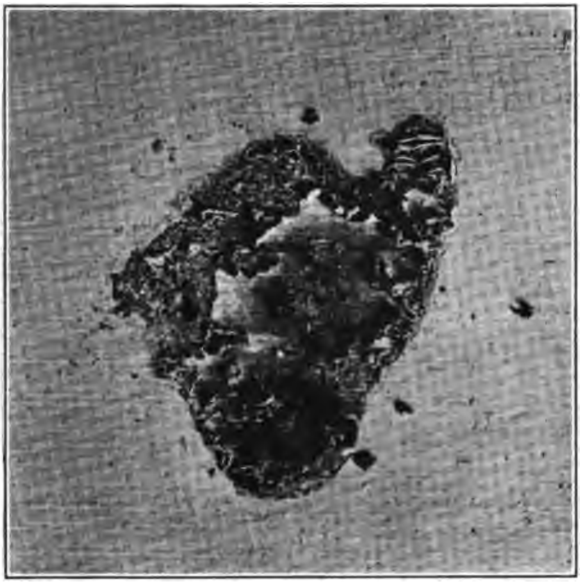
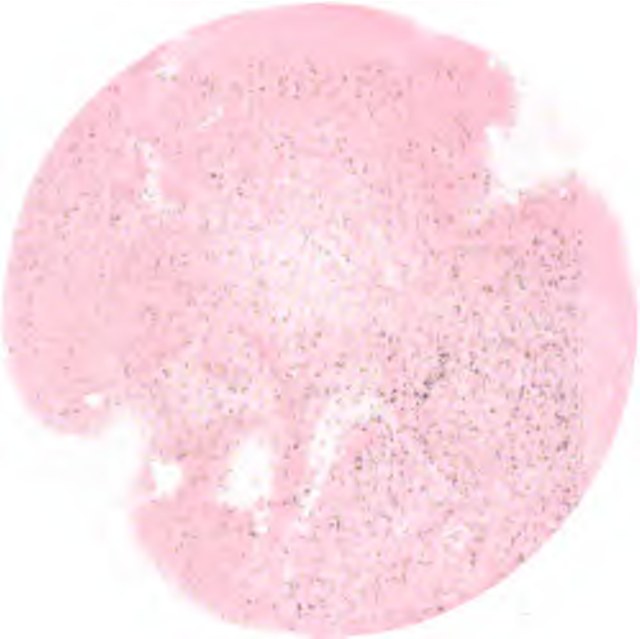


FIG. 129.
Effect of Black Fungi upon Soft-drying Paint.

Some of the paints applied were made of lead and some of lead and zinc pigments. In every instance lead was found present, zinc being detected in the washings from some zinc-containing paints.

Attention has been brought to the fact that the washing of paint is not of uniform occurrence. It may be noticed upon the porch columns but not upon the body and trim of a house, or it may be noted only upon certain sections of the main structure. The writer has observed that in most instances

FIG. 130.



Pink mould growing from "foots" of infected oil.

(Species of Fusarium.)

where washing is shown it is generally upon a hollow column or surface, the back of which may hold moisture. It is likely that the moisture stored up in certain places is responsible for starting the complicated reactions which have been previously referred to. It is also possible that the painter, when making up various batches of paint, may use in one batch that portion of the oil which contains the largest quantity of foots and moisture. The section upon which this batch of paint is used would, of course, show the greatest amount of washing. That such types of washing are periodical could be explained by the fact that infected seed occurs in quantity only in such years as the flax crop is poor. In the writer's opinion, the prevention of such trouble lies in the use of a well-filtered, perfectly-clarified, moisture-free oil. Washing may also occur on the side of a painted structure that is exposed to a rain storm during the drying of the paint. Under such conditions the exposed side would absorb water which would emulsify the drying paint and result in washing. The other unexposed sides might dry up hard and give satisfactory results. Painting in damp weather is always dangerous. The vapor pressure

FIG. 131.

Lumber Mill Showing Log Pond. (See Text.)

being high naturally slows down the evolution of volatiles from the paint, retards oxidation and probably will be responsible for many cases of washing.

"Rusting" or Brown Spotting.—Another painting defect, the cause of which may be traced in some instances to the action of microörganisms or their products, is the so-called "rusting" or brown spotting of paints. This condition is generally noticed upon the ceilings of porches, small brown spots about a quarter of an inch in diameter appearing through the paint film like resin exudations. These spots have an astringent acid taste. This condition, moreover, is generally found upon jobs where the type of washing of paint previously referred to has been recorded, thus indicating that the trouble might be of similar origin. Several of these small, brown-colored spots which appeared upon painted surfaces were recently collected and examined. In some instances these drops were shown by chemical analysis to contain resinous ingredients, and in other instances metallic substances in combination with organic products. They are generally very soluble in water, yielding

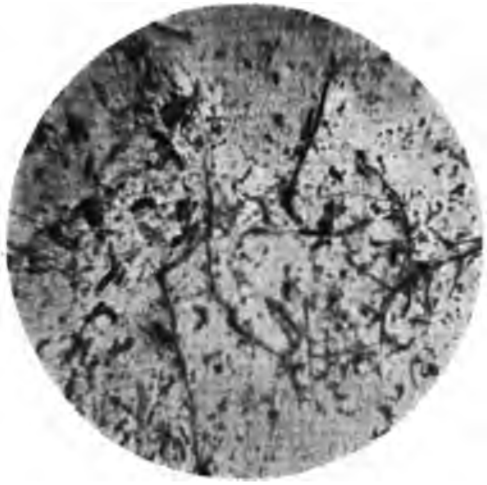


FIG. 132.

Mycelium and Spores of the Pink Mould. × 1400.

rather thick, viscous solutions upon boiling and filtration. When the paint is made of lead, organic salts of lead are found in the solution. If zinc is present in the paint, zinc salts may also be found by analysis. As a result of the investigation, the writer is firmly convinced that the formation of these drops may be traced to two distinct causes. In some instances the soluble matter contained in the wood may be brought to the surface, exuding at certain places in the paint film and drying up to small, round globules. In certain types of wood there are exceptionally large amounts of soluble constituents which may appear, especially in damp weather and upon surfaces which are not exposed to the sun. Such water-soluble substances apparently have a solvent effect upon the lead and zinc contained in a paint, the compounds formed being deposited upon the surface of the paint in the form of globules. This condition, however, would occur only upon new wood. When wood has been painted for three or four years, it has weathered to such an extent that the water-soluble materials are pretty well leached out. It has been found, however, that brown spotting occurs most often upon repainting jobs, especially when the oil used in the paint has been of the type examined by the writer, containing moisture and foots of an infected nature. In such cases the hydrolyzing action of the enzymes, which takes place when such oil is used, aparently increases the tendency of the oil to break up into various fatty acids, including formic acid. This has a solvent effect upon the lead and zinc pigments, producing lead and zinc formates which are water-soluble and possessed of an astringent taste. It is therefore likely that such water-soluble metallic compounds, when produced, come as the result of reactions within the oil itself in many instances, and would again indicate the necessity of using properly-clarified oil. The writer has previously pointed out that proper weathering of new wood before painting will largely do away with the type of spotting that comes from the water-soluble constituents of such wood. It is apparent, however, that the selection of satisfactory oil is an even more important consideration, especially upon repainting work.

Immunization of Oils.—Assuming that some types of oil* may even be responsible for defects developing in paints while in storage and previous to use, the question of immunization is one worthy of consideration. Although the writer has previously shown that sterilization of the oil is possible by the application of heat, this procedure may not be feasible in many instances. The same effect, however, may often be produced in the paint mill under ordinary manufacturing processes. It is well known that considerable heat is developed when mixtures of oil and pigments are run through buhrstone mills, the temperature of the paint depending upon the rate of grind-

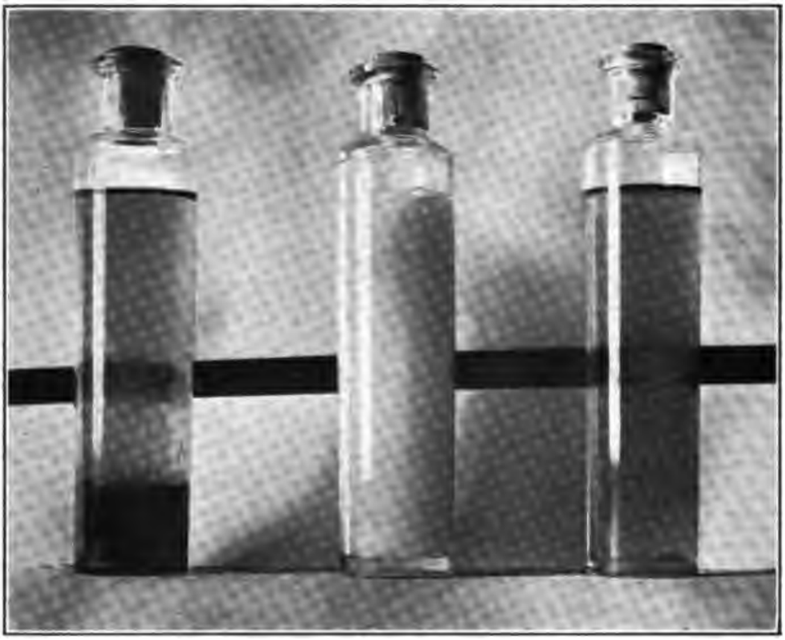


FIG. 133.

Three samples of linseed oil. Black line in back of bottles shows relative clarity. Oil in middle bottle contains considerabe moisture and "foots." Oil in end bottle contains a large amount of infected "foots" deposited at bottom.

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* "Changes Occurring in Oils and Paste Paints, Due to Autohydrolysis of the Glycerides," p. 286.

ing and set of the plates. Temperatures up to 240° F. have even been recorded, and this is more than sufficient for sterilization. It is probable that many oils have thus been rendered harmless, whereas they might have caused trouble had they been mixed cold with hand paddles. Moreover, the hot paste paint as it issues from a mill is in a condensed form, unobtainable by hand stirring. The writer has recently made a study of the chemical phenomena which may result from the storage of such paints in their warm condition. In one instance the hot paste was immediately thined and canned. In another instance the paste was allowed to cool before thinning and canning. In the latter case the paint proved to be in the most satisfactory condition after storage. When the hot paste is immediately canned, the continued warmth of the product is apt to set up slight hardening with certain pigments. It is probable, however, that the use of a water-cooled spout at the point of exit from the mill plates would sufficiently cool the issuing paste so that storage before canning would not be necessary.

Conclusion.—From the previous considerations it is apparent that many painting defects may be prevented through the use of paints of the composite class, based upon white lead pigments but containing sufficient zinc oxide to present a firm, hard film.

When paste paints are thinned by the painter, only clarified, well-settled, moisture-free linseed oil should be used. Exterior painting should always be done in dry weather if defects, such as washing, are to be avoided.

CHAPTER XIX.

CHANGES OCCURRING IN OILS AND PASTE PAINTS, DUE TO AUTO-HYDROLYSIS OF THE GLYCERIDES.

In seeds of the oil-producing type, enzymes are known to exist, which have fat-splitting properties and which exert a marked influence upon the metabolism of the growing plant. That these enzymes may continue their action, even when the oil from the seed is used for some commercial purpose, has probably never occurred to the student of paint technology. In previous investigations,* the writer has referred to the possibility of oil hydrolysis by enzymes, and has described the hardening action of free fatty acids upon various pigments. As a result of more recent work, the writer is convinced that many of the phenomena referred to are due to the action of enzymes. The data presented below include suggestive measures for preventing such action.

A majority of paints are made of linseed oil (pressed from flaxseed) as the chief constituent of the vehicle or liquid portion. Plant pathologists have recently shown that flaxseed is sometimes infected by a certain type of wilt or micro-organism which prevents the proper development of the plant resulting from the growth of the seed. The yield and character of flaxseed produced by such plants are low and unsatisfactory. It is probable that crushers have at times received shipments of such seed, especially during years when small crops were obtained. When such seed is crushed for its oil content, part of the micro-organisms in the seed passes into the oil. The sediment or "foots" present in all raw oil is made up largely of mucilaginous and nitrogenous matter which affords an ideal sprouting medium for micro-

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*Formation and Inhibition of Mildew in Paints, p. 264.
The Effect of Pigments upon the Constants of Linseed Oil, p. 294.
The Effect of Pigments Ground in Linseed Oil. Journal Ind. and Engrg. Chem., September, 1911.

organisms. The small percentage of moisture present in raw oil is also favorable to their growth.

Flaxseed is usually steamed, previous to expression, in order to break up the oil cells and render the expression more complete. This steaming process is usually conducted at relatively low temperatures which do not destroy the micro-organisms present. Spores may therefore be left in the seed, which may later develop micro-organisms identical with those present before the steaming process. These micro-organisms require food for their continued growth. In order to obtain such food, they evolve certain enzymes which have fat-splitting properties. It is the writer's belief that, under favorable conditions, the enzymes evolved by the micro-organisms present in crushed linseed oil energetically attack the oil and split it up into its component parts—free fatty acid and glycerin. Both of these substances are foods for certain types of micro-organisms. A freshly crushed linseed oil, of normal acid value of approximately 4, may contain enzymes capable of splitting up the oil and thus greatly increasing the acid value within a short time. If such oil is used in a paint containing basic pigments, trouble may ensue. After the oil has been split up, the fatty acid formed will react with the basic pigments and form metallic soaps which are not only insoluble in paint but which become annoying on account of their peculiar character. If the reaction has been strong and extended over a long period of time, difficulty may be found in brushing out such paint to a perfectly smooth surface.

The writer recently examined a paste lead paint which was very granular in condition, and, as a result of the examination, is inclined to the opinion that the oil used in the paint was expressed from infected seed. This oil probably contained enzymes which split up the oil into its two component parts. The basic pigments in the paint neutralized a portion of the fatty acids which were set free, and thereby formed little lumps of insoluble fatty acid soaps which were apparently made up of the higher fatty acids. Another paste paint was examined and found to be very lumpy. The lumps could not be brushed out to a smooth surface. Some had the appearance of dried bits of paint skins. Others resembled lumps of wax. These lumps, upon analysis, were separated into a liquid fatty acid having an acid value of approximately 180, a solid fatty product having an acid value of 84, and a metallic pigment which was present in combination with a part of the organic acid as a metallic soap. The micro-organisms in the oil paint may have had a selective action upon the lower fatty acids, thus leaving a concentration of the higher and more active fatty acids to combine with the basic pigment in the paint.

Previous to this investigation, the writer had obtained a sample of linseed oil which had given much trouble to pigment grinders. When this oil was used in making white lead paints, considerable thickening occurred after six months or a year.

The oil was very cloudy in appearance. The following analytical results were shown:

Specific gravity	.9450
Iodine number	171.3
Saponification number	133.2
Acid number	4.1
Foots (per cent.) by volume	9.0
Moisture and volatile matter (per cent.)	.68

The "foots" present had an acid value of 6.9. After clarification, by repeated centrifuging, the oil gave the following constants:

Iodine number	177.3
Saponification number	190.2
Acid number	3.9

A sterile platinum needle was dipped into the "foots" obtained from the above-described oil, and an extremely minute quantity was placed separately upon sterile agar-agar, gelatin and beef bouillon contained in test tubes. The tubes were placed in an oven at 37°. At the end of 24 hours there was shown in each test tube a most marked development of white mould. Some of the incubated bouillon culture was then plated out upon agar-agar in petri dishes and again incubated at 37° for 24 hours. At the end of that time the surface of the agar was covered with micro-organisms which were growing in profuse quantities (Fig. 134). Some of these were transferred to a microscopic slide, stained, and examined with an oil immersion lens. A distinct form of bacilli was plainly shown (Figs. 135 and 136). In appearance, the bacilli were similar to the hay bacillus which is known to exist in some kinds of grain.

A portion of the above-described oil was then mixed with corroded white lead and thoroughly ground to a smooth, heavy paste. The paste paint was placed in an oven heated to 37° C. and allowed to remain there for one week. At the end of that time an examination of the paint showed a few tiny granules, indicating that some reaction had taken place. A portion of the oil was extracted and its acid value found to be two points higher than that shown by the original oil, thus indicating hydrolysis. The presence of mere traces of acetic acid, free carbonic acid and moisture in white lead may have had an accelerating influence on the action of the enzymes. Such impurities probably act in a catalytic manner. Under favorable conditions, and with several weeks' time for

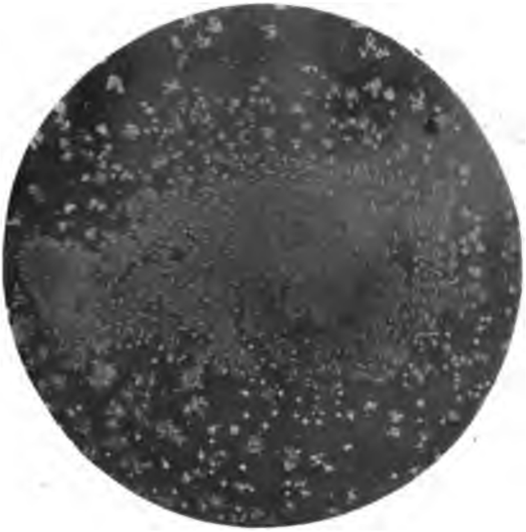

FIG. 134.

Colony of Bacilli Obtained from Oil "Foots" Growing on Agar-agar.

reaction, much greater hydrolysis would have taken place. Within a year or two the lead paste might have become very granular. An experiment was then conducted to determine the effect of the micro-organisms present in the cloudy oil, when allowed to react with oils known to be free from such micro-organisms. A portion of the cloudy oil, which had shown a marked development of mould, was mixed with a sample of pure linseed oil of known acid value. A few drops of water containing carbon dioxide gas were added. The acid value of the mixture was determined. At the end of forty-eight hours the acid value of the oil mixture was 10 per cent. greater than before.

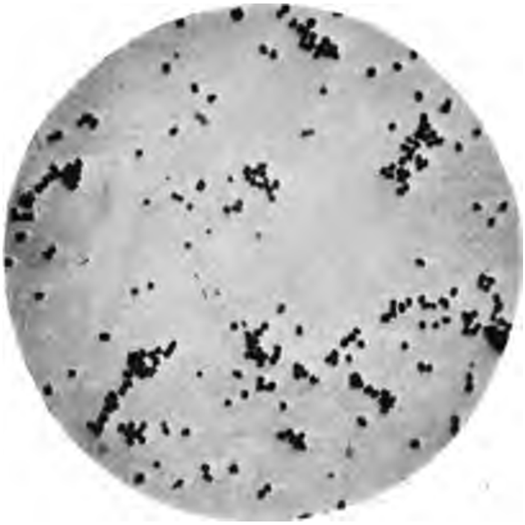

FIG. 135.

Mould Spores Obtained from "Foots" of Infected Oils. × 1200. Oil Immersion Lens. Green Light Filter.

Some experiments were then made to determine whether the bacilli in the cloudy sample of linseed oil could be destroyed by adding small quantities of antiseptic substances. The oil was distributed in test tubes and treated with small percentages of antiseptics such as cresol, carbolic acid, salicylic acid, sodium benzoate, etc. Sterile agar was then inoculated with these samples of oil, and incubated. At the end of twenty-four hours a development of mould was shown upon each, thus showing that the above-named powerful antiseptic substances had not destroyed to any marked extent the micro-organisms present in the oil.

An attempt was then made to determine whether the micro-organisms could be destroyed by heat. Samples of the cloudy oil were heated individually to 100°, 150°, and 200° C. As soon as the maximum temperature was reached, the oil was immediately allowed to cool. By this process the constants of the oil were not changed to any material extent. Test tubes containing agar were then treated with these heated oils. At the end of periods of twenty-four hours, forty-eight hours, seventy-two hours, and one week, absolutely no development of mould was shown. Bacilli could not be found in the incubated agar. These experiments indicate that the presence of micro-organisms in linseed oil which comes from poor seed, may be destroyed by rapidly heating the oil to 100° C.,

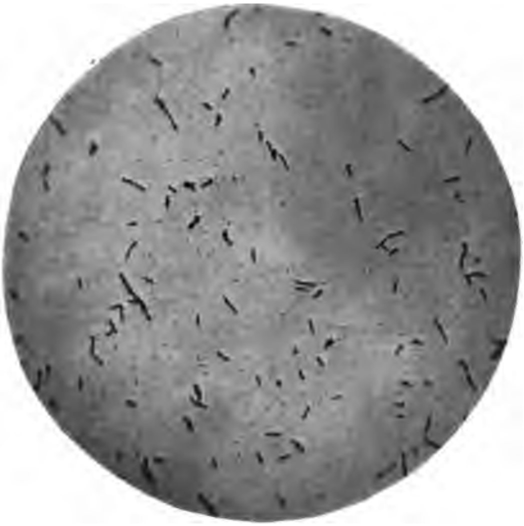

FIG. 136.

Bacill Obtained from "Foots" of Infected Oil. × 1200.
Oil Immersion Lens. Green Light Filter.

immediately withdrawing the heat to prevent oxidation, and allowing to cool. This heating process has the added advantage of rendering the oil clearer and better suited for general purposes. During the past, some manufacturers have used refined oil which has probably been heated during the process of refinement to the critical temperature noted above. For this reason, paints made of such oil have not deteriorated. On the other hand, some manufacturers have used raw oil which has not been refined or heated to 100° C., and such oil in some instances has probably been responsible for the granular condition observed in the lead paste.

It is interesting in this connection to record the condition of several prepared paints which were recently examined by the writer. These paints had been found among an old stock of supplies. They were packed in 1898. After sixteen years, no lumping, hardening or granulation had taken place. They were in perfect condition. Both lead and zinc whites were used in the pigment portion. The result of this examination would indicate that properly prepared paints made of good oil are capable of remaining in good condition for many years in sealed packages.

After making the above-outlined experiments, the writer made a search of the literature bearing on the metamorphosis of oils, and found several instances of the development of fatty acids in abnormal amount. Crampton* examined butter that had been kept in his laboratory for three years. The acid value had risen in that time from 5 to 109. He attributes this change to the action of moulds which were identified as Coniosporium and Penicillium (?). Similar experiments on butter were conducted by Koenig, Spiechermann and Bremer,† who attribute the action to enzymes evolved. Lewkowitsch‡ refers at length to the fat-splitting properties of enzymes, and points out the better keeping properties of lard rendered by steam at 100° to 120° C. as compared with neutral lard rendered at a low temperature not sufficient to destroy all of the enzymes present. Lewkowitsch also refers to the rancidity developed in a sample of palm oil, which had been kept away from light and air, as proving that enzyme action can take place in oils stored in closed containers.

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* Journal Amer. Chem. Soc., 1902, 24-711.

† Zeitschrift Unt. Nahr. und Genussmittel, 1900, 3-606.

‡ Chemical Technology and Analysis of Oils, Fats and Waxes. Lewkowitsch. Vol. I, 37-38.

It has occured to the present writer that the rancidity of many oils could be prevented by inhibiting enzyme action. For instance, it is quite possible that the odor of fish oils is due to the development of evil-smelling free acids developed by enzyme action. If fish oils were treated immediately after pressing, it is possible that better-smelling products could be produced from marine animals. That the study of enzyme action should extend to other oils used in the manufacture of paint and varnish seems to the writer as most important. Many of the peculiarities of such oils as tung and lumbang might receive more satisfactory explanation as a result of studies. It is also possible that new light might be thrown upon the interesting subject of oil synthesis.

In summing up the results of the present work, the writer would call the attention of the oil crusher to the advisability of heating raw linseed oil to at least 100° C. previous to shipment. Oil which has been treated in such fashion is "immune," or "sterile," and will therefore be found much more satisfactory for grinding basic pigments having a lead or zinc base. The writer would also call attention to the necessity of using well-filtered oils. Oils having a large percentage of "'foots" are always dangerous to use with basic pigments.

CHAPTER XX.

THE EFFECT OF PIGMENTS UPON THE CONSTANTS OF LINSEED OIL.

When sealed packages of paints of the cheaper grades are opened after having been stored for a considerable length of time, there is occasionally observed a degree of hardness that renders application difficult. The user is generally at a loss to account for such a condition, inasmuch as the modern metal container is air-tight and has but little room for improvement. The cause of the hardening that has taken place may therefore be assumed to result from certain reactions between the different constituents of the paint. There can be no doubt but that certain kinds of pigments have some influence in the reactions that result in hardening, but the responsibility has been too often placed entirely with the pigment portion of paints. That the oil or vehicle part may have an even more profound relation to the trouble has not been given the consideration it deserves. In support of this statement there is presented herewith evidence of an important nature, in the form of results obtained from the tests described below.

Early in 1911 the writer carefully prepared a series of paints from various well-known pigments, using as a grinding medium a standard vehicle of pure linseed oil containing neither drier nor thinner of any type. The amount of oil used with each pigment was sufficient to bring the paints in every case to relatively the same viscosity or body, which was somewhat heavier than is ordinarily used in the application of paints to wooden or metal surfaces. These paints, after preparation, were carefully placed in friction-top tin containers. They were moved about occasionally and were subjected to shipment by freight on two occasions, finally remaining on a shelf in the writer's laboratory for nearly a year previous to examination. Upon removing the lids from the cans there was evidenced, by the appearance of some of the paints, a considerable change of a chemical nature. The writer, attributing the change that had taken place to a form of saponification, or rather hydrolysis, as such action may be properly termed in the case of paints, was impressed with the opportunity of examining the oil content of the paints, in order to determine whether any marked change had occurred in the constants of the pure linseed oil which was used in their grinding. Fortunately, there was on record the analysis of the oil which had been used for this purpose. The liquid part of each paint was separated from the pigment portion and the oil was obtained and submitted to examination. The results of these tests are given below.

RESULTS OF EXAMINATION OF OILS EXTRACTED FROM PAINTS.

Analysis of Oil Used in Grinding and Thinning Paints:

Specific gravity	.932
Ash	.190%
Iodine No.	181.
Acid value	2.5

Test No. 1.

Zinc Oxide.

Condition on Opening.—Paint in excellent condition. Very soft. Some oil of light color floating on top. After extraction with solvent the oil contained fine white zinc of a colloidal nature, which separated out only after several days' standing.

Analysis of extracted oil:

Specific gravity	.9237
Ash	0.36% (white)
Iodine No.	161.
Acid value	3.5

Test No. 2.

Corroded White Lead (Basic Carbonate-White Lead).

Condition on Opening.—Paint had thick, wrinkled skin on top, but was in very fair condition. Oil, after extraction, was light colored and clear.

Analysis of oil:

Specific gravity	.9372
Ash	1.149% (light yellow)
Iodine No.	157.5
Acid value	8.6

TEST No. 3.

Leaded Zinc.

Condition on Opening.—Paint in very good condition. Considerable oil floating on top. Oil, after extraction, was somewhat cloudy, but cleared up after settling for twenty-four hours.

Analysis of oil:

Specific gravity	.9389	
Ash	.922%	(white)
Iodine No.	157.4	
Acid value	5.7	

TEST No. 4.

Corroded white lead (basic carbonate-white lead)	50%
Zinc oxide	40%
Barytes	10%
	100%

Condition on Opening.—Paint in excellent condition. Some oil floating on top.

Analysis of oil:

Specific gravity	......	
Ash	.674%	(light yellow)
Iodine No.	154.1	
Acid value	6.7	

TEST No. 5.

Sublimed white lead (basic sulphate-white lead)	60%
Zinc oxide	40%
	100%

Condition on Opening.—Paint in excellent condition. Some oil floating on top.

Analysis of oil:

Specific gravity	.9334	
Ash	.626%	(white)
Iodine No.	157.8	
Acid value	5.6	

Test No. 6.

Barytes (Barium Sulphate).

Condition on Opening.—Paint settled to a considerable extent. Much clear oil floating on top.

Analysis of oil:

Specific gravity	.9325
Ash	.212% (light)
Iodine No.	160.6
Acid value	3.5

Test No. 7.

Silica.

Condition on Opening.—Heavy, viscous oil, resembling a varnish, was floating on a partly-settled mass of pigment. After extraction, the oil held some finely-divided pigment in suspension for some time.

Analysis of oil:

Specific gravity	.9465
Ash	.204% (light)
Iodine No.	149.2
Acid value	8.7

Test No. 8.

American Vermilion (Basic Chromate of Lead).

Condition on Opening.—Pigment settled very hard. Oil, after extraction, was dark, but clear.

Analysis of oil:

Specific gravity	.939
Ash	1.271% (yellow)
Iodine No.	156.7
Acid value	8.3

Test No. 9.

Red Lead.

Condition on Opening.—Pigment settled very hard. A thick, gelatinous oil floating on top of pigment. Oil, after extraction, was dark brown in color.

Analysis of oil:

Specific gravity	....
Ash	15.56% (light red)
Iodine No.	135.4
Acid value	19.2

TEST No. 10.

Iron Oxide.

Condition on Opening.—In excellent condition. Very soft, smooth paste. After extraction, the oil was clear, but of a dark red color.

Analysis of oil:

Specific gravity	.9457
Ash	.456% (red)
Iodine No.	156.3
Acid value	8.6

TEST No. 11.

Carbon Black.

Condition on Opening.—Thin, wrinkled skin on surface. Paste below skin very soft and smooth. After extraction, the oil was clear and of light color.

Analysis of oil:

Specific gravity	.9356
Ash	.195% (light)
Iodine No.	163.
Acid value	10.5

TEST No. 12.

Graphite.

Condition on Opening.—Very soft and smooth paste. After extraction, the oil was clear and light in color.

Analysis of oil:

Specific gravity	......
Ash	.201% (light)
Iodine No.	158.5
Acid value	13.3

These results show that inert pigments such as barytes, iron oxide, graphite and carbon black do not enter into chemical action with linseed oil; the percentage of ash found in the oil extracted from the above pigments being practically identical with the percentage shown by the raw oil. That such pigments may, however, have some physical action upon the oil, that will later develop a chemical change therein, seems evident. The thickened condition of the oil extracted from the silica paint, and the low iodine values and high acid values shown by all of the oils extracted from the above-mentioned inert pigments, would give credence to the above statement.

The pigment that is ordinarily termed American vermilion, the true form of which is a basic chromate of lead, seems to have had no very marked effect upon the oil in which it was ground. It would seem, therefore, that it would prove quite practical to transport this pigment in paste form. On account of its value as a protective of metal, it will probably replace, to some extent, the use of red lead for priming steel. The pigment red lead had a marked hydrolyzing reaction on the oil in which it was ground. The latter contained a very large percentage of lead linoleate, free fatty acid, and glycerin. The iodine number of this oil was lower than that of any other extracted. It is, of course, well known that red lead, on account of its tendency to harden in the package, is seldom put up in mixed form. The dry pigment is generally mixed with oil just before application, from 30 to 35 pounds of pigment to a gallon of oil being the proper consistency for painting.

Zinc oxide and zinc lead had but slight action with the oil, while basic carbonate-white lead showed somewhat greater action, but not sufficient to be of any detriment. With paints containing mixtures of lead and zinc pigments only slight action was shown. The perfect condition of these paints indicates that any properly-prepared combination pigment paint may be safely stored in cans for long periods without bad effects, provided the oil used is of normal grade.

The most surprising change shown in the tests was that in the iodine values of the oils extracted from all of the paints. It would appear, therefore, that when paints are stored for a considerable period of time and then examined for the iodine value of their oil content a lowering of the iodine value should not constitute cause for rejection or be sufficient evidence to state that the oil was adulterated with oils of lower iodine value. Cognizance of this statement should be given by railroads and purchasing corporations which have adopted specifications for oil paints.

As is well known, linseed oil is a mixture of tri-glycerides of fatty acids. In other words, fatty acids are combined with glycerin in the proportion of three equivalents of acid to one equivalent of glycerin, the latter material acting as a tri-atomic alcohol or base. The fatty acids in linseed oil, among which may be mentioned oleic acid, are of an unsaturated nature, being capable of taking up large quantities of oxygen. The combination of these fatty acids with glycerin may be effected by certain enzymes which exist in the seed of the plant. Moreover, the resolution of such compounds with a consequent breaking away of the acids from the glycerin, to a free condition, may be accomplished by enzymes which have hydrolyzing properties. This splitting-up reaction may also be effected by several methods of a chemical nature. The hydrolyzing effect of moisture is sometimes of considerable moment and is probably responsible to some degree for the small percentage of free fatty acid which is generally present in all linseed oils. That some oils have higher acid values than others is well known, the acid refined oils being especially high in free acid; treatment with various mineral acids accelerating hydrolysis. The most rapid form of hydrolysis is effected with strong bases such as soda, the ultimate products being water-soluble soda soaps and glycerin. When the hydrolyzing base is a relatively insoluble product and of a metallic nature such as litharge, the hydrolysis of the oil is slow and only partial, there being formed a water-insoluble lead soap, glycerin, and some free fatty acid.

When hydrolysis has taken place in a paint, considerable thickening is observed. In the tests which are charted above it will be observed that the most extravagant example of hydrolysis was shown by the red-lead paint. The oil from this paint showed over 15 per cent. of inorganic lead compounds in the ash. It will also be noticed that the oil had become very acid in nature and had the appearance of a thick jelly. Although the red-lead paint was very thick, difficult to break up, and too heavy for brushing, it was not really hard. The writer has had occasion, however, to examine several samples of paint recently which were very much harder than the red lead, one, in fact, being so hard that a knife was required to make any impression upon its solidified surface. These paints, moreover, contained pigments of a basic nature, containing a very high percentage of lead and zinc. An examination of the oil in which these paints were ground showed acid values ranging from 8 to 16. That the reaction of the free acid upon the pigments was the real cause of the hardening of the paint was the writer's conclusion. A series of tests were therefore made, in which was included the treatment of paints with small percentages of free oleic acid, one of the most prominent constituents found in oils of a high acid value. There were also included tests in which paints were treated with sulphites, there existing in the paint industry a false belief that lead and zinc pigments are apt to body and harden in oil if they contain even traces of sulphur dioxide or sulphites. Those who have held such a belief should some time examine paints made of sublimed blue lead, a pigment which contains nearly 5 per cent of metallic sulphites and sulphides. This pigment will remain as a smooth paste in oils for months without any apparent hardening.

Small quantities of dry zinc and lead pigments (basic carbonate-white lead, basic sulphate-white lead, zinc oxide, and zinc lead) were ground in a pure raw linseed oil having a normal acid value of approximately 2.8. After standing for three days, no tendency toward hardening was shown by any of the paints. They were then divided into small portions, and to each type were added various materials which were under suspicion as having, when used, some contributing effect in the hardening of paint. The following table shows the results of these experiments:

Treatment with 20 per cent. gloss oil (½ rosin, ½ benzine).....	Considerable hardening shown in 24 hours, indicating action between the acid rosin (resinic acids) and the basic pigments.

Treatment with 2 per cent. sodium hyposulphite	No effect noticed in 6 days.
Treatment with 5 per cent. oleic acid	Hardening occurred in two hours and increased with age. Paint resembled hard putty.

From these results it is apparent that oils of an acid nature are the most active cause of paint hardening. The use in cheaper paints of substitutes for linseed oil, which contain large percentages of rosin, as well as the promiscuous use of acid rosin driers, has been the cause of the hardening of many paints. Linseed oil containing high percentages of acid is, of course, dangerous. It is evident, therefore, that a careful consideration of the vehicle portion of a paint is even more important than the pigment part, and a careful record of the acidity of paint oils should be kept by the grinder.

CHAPTER XXI.

STORAGE CHANGES IN VEGETABLE AND ANIMAL OILS.

The writer's attention has recently been called to instances where linseed oil that has been separated from paints has shown low chemical constants. In one instance, several barrels of paint made of pure raw linseed oil stood in a factory yard for a few weeks, exposed in the daytime to the sun. A temperature of 115° F. was probably reached in the middle of the day. Upon analysis, the consumer found the oil that was separated from the paint to have a lower iodine number than that called for by the specifications. The shipment of paint was accordingly rejected. Since pure linseed oil of the proper iodine number was used in the paint, it is apparent that hydrolysis occurred on storage. That such changes are possible should, therefore, be considered by the testing engineer when examining the vehicles of specification paints that have not been freshly used.

The writer has previously pointed out the degree of change which may be expected to take place in linseed oil when ground with various pigments, and he has also indicated the contributing effects of impurities in oils. Some more recent work has shown that nearly all oils, even when not in contact with pigments, will show changes in their chemical constants when allowed to stand for a period of time. The drop in iodine number is generally accompanied by a rise in specific gravity and acid value.

Quantities of a number of oils were obtained by the writer several years ago for use in the exposure tests made at Washington to determine the wearing properties of such oils when used in paints. Analyses of these oils at various periods are shown in the attached tables.

TABLE 25.

ANALYSES OF OILS.

Analyses were made when oils were first obtained and 44 months later, at the time they were used in repainting tests. The oils were again analyzed 22 months later, in September, 1916. Chemical changes occurring in the oils are denoted by the constants.

	Sp. Gr.	Iodine No.	Sapon. No.	Acid No.	Refrac. Index.
Raw Linseed Oil—					
March, 1911	.931	186	188	2.0	......
November, 1914	.933	185.4	189.6	2.8	1.4867
September, 1916	.936	176.9	190.2	3.3	1.4798
Soya Bean Oil—					
March, 1911	.924	129	189	2.3	......
November, 1914	.925	130.2	193.1	4.7	1.4813
September, 1916	.937	122.0	192.1	7.0	1.4733
Menhaden Oil—					
March, 1911	.932	158	187	3.9	......
November, 1914	.934	156.3	193.7	16.1	1.4850
September, 1916	.938	144.9	191.4	19.2	1.4768
Raw Tung Oil—					
March, 1911	.944	166	183	3.8	......
November, 1914	.946	161.5	190.3	5.7	1.5050
September, 1916	.944	158.6	188.7	5.6	1.5138
Perilla Oil—					
March, 1911	.94	180	188	2	......
November, 1914	.94	172	195.4	7.4	1.4874
September, 1916	.939	160.9	193.3	14.8	1.4767
Perilla Oil (Special)*—					
March, 1911	.94	192	189	3.2	......
November, 1914	.981	123.8	219.4	20.8	1.4978
September, 1916	1.000	122.4	220.9	31.2	1.4840
Heavy-bodied Linseed Oil—					
March, 1911	.968	133	189	2.8	......
November, 1914	.992	130.5	200	6.3	1.4966
September, 1916	....	124.4	206.3	9.0	1.4876
Lithographic Linseed Oil—					
March, 1911	.97	102	199	2.7	......
November, 1914	.96	103.4	150.9	13.4	1.4978
September, 1916	.974	108.5	137.7	15.2	1.4890
Whale Oil—					
March, 1911	.924	148	191	9.2	......
November, 1914	.926	138.2	191.2	17.4	1.4820

*Has become highly viscous.

TABLE 25—Continued.

	Sp. Gr.	Iodine No.	Sapon. No.	Acid No.	Refrac. Index.
Boiled Linseed Oil—					
March, 1911	.941	172	187	2.7	......
November, 1914	.943	170	188	3.1	1.4895
Corn Oil—					
November, 1914	.921	124.8	190.1	4.1	1.4800
September, 1916	.924	121.3	191.1	4.6	1.4707
Cottonseed Oil—					
November, 1914	.920	111.7	194.3	0.9	1.4781
September, 1916	.924	110.6	192.9	1.4	1.4681
Rosin Oil—					
November, 1914	.964	68.9	35.5	32.4	......
September, 1916	.964	66.0	36.6	31.6	......
Treated Tung Oil*—					
November, 1914	.882	56.4	101.3	7.7	1.4764
September, 1916	.884	53.2	103.2	8.0	1.4660
Lumbang Oil—					
November, 1914	.927	162	189	1.0	1.4789
September, 1916	.926	164.0	188.9	1.9	1.4748
Sunflower Oil—					
November, 1914	.924	124.6	189.3	7.5	1.4796
September, 1916	.923	122.2	190.2	9.0	1.4712
Hempseed Oil—					
November, 1914	.927	149.4	191.1	3.9	1.4822
September, 1916	.930	146.1	191.0	5.0	1.4745
Shark Oil—					
November, 1914	.910	132.8	158.9	5.2	1.4815
September, 1916	.915	127.4	163.3	6.2	1.4722
Sardine Oil—					
November, 1914	.919	134.6	177.3	10.4	1.4800
September, 1916	.962	91.4	180.2	31.1	1.4755
Petroleum Oil—					
November, 1914	.851	28.2	52.9	1.1	1.4773
September, 1916	.850	28.0	48.6	1.0	1.4669

*Heat treated with driers and thinned with mineral spirits.

TABLE 26.

EFFECT OF STERILIZATION ON OILS.

Original oil analyzed in November, 1914. Individual portions placed in separate bottles. One set of bottles sealed and heated to 110° C. Both sets again analyzed in September, 1916.

	Sp. Gr.	Iodine No.	Sapon. No.	Acid No.	Refrac. Index.
Raw Linseed Oil—					
November, 1914........	.933	185.4	189.6	2.8	1.4867
September, 1916........	.936	176.9	190.2	3.3	1.4798
Sterilized—Sept., 1916..	.934	187.1	190.4	3.1	1.4776
Sunflower Oil—					
November, 1914........	.924	124.6	189.3	7.5	1.4796
September, 1916........	.923	122.2	190.2	9.0	1.4712
Sterilized—Sept., 1916..	.925	124.6	189.9	6.3	1.4696
Menhaden Oil—					
November, 1914........	.934	156.3	193.7	16.1	1.4850
September, 1916........	.938	144.9	191.4	19.2	1.4768
Sterilized—Sept., 1916..	.937	155.6	192.1	16.3	1.4782
Perilla Oil—					
November, 1914........	.94	172	195.4	7.4	1.4874
September, 1916........	.939	160.9	193.3	14.8	1.4767
Sterilized—Sept., 1916..	.941	174.3	194.2	12.6	1.4788

TABLE 27.

RAPID HYDROLYSIS OF LINSEED OIL EMULSIONS.

Equal parts by volume of water and oil emulsified with 1 per cent neutral gum. Emulsions kept in incubator at 20° C. for 45 days. At this temperature, in the presence of water, and with a possibility of the accelerating action of enzymes, oils have rapidly developed free acid.

	Acid value.				
	April 1.	April 6.	April 18.	May 4.	May 16.
1. Raw	2.1	3.0	5.6	6.0	8.4
2. Raw—Sterilized	2.1	2.5	2.6	4.6	6.2
3. Alkali Refined...........	1.6	2.4	2.4	6.6	....
4. Acid Refined	15.6	15.8	24.8	35.8	44.8
5. Acid Refined............	3.0	4.0	15.0	34.0	38.0
6. Boiled	4.6	7.4	13.6	22.0	38.8

CHAPTER XXII.

PAINT DRIERS AND THEIR APPLICATION.

Driers.—The drying of oils and their behavior with various siccatives in varying quantity is an interesting problem, and, obviously, of considerable importance from a practical standpoint. Unfortunately there is a decided scarcity of reliable literature dealing with the subject for the guidance of those concerned in the manufacture or application of siccative products. Furthermore, when the problem is investigated, it is not difficult to see why this is so.

At a glance, it is evident that a decided obstacle in experimentation on the drying properties of oils, is the difficulty in obtaining identical conditions for comparative purposes. Inasmuch as a multitude of factors, such as uniformity and homogeneity of the driers and the oils themselves, intensity and source of light, temperature, uniformity of application, and many others, play a decisive part in the drying tendencies of oils, the resources and ingenuity of the chemist engaged in the research are taxed.

It is a well-known fact that linseed oil, when applied to a clean surface, such as a glass plate, will undergo oxidation and take up oxygen to the extent of about 16 per cent., forming a hard, elastic, non-sticky product which has been called linoxyn. This material, unlike the oil from which it has been formed, is insoluble in most solvents. Other oils, such as cottonseed, hemp, rape, olive, etc., are more fully satisfied in nature and have not the power to absorb the amount of oxygen taken up by linseed oil. Perilla oil, however, may absorb as high as 20 per cent. of oxygen.

In carrying out the following tests, on the drying of oils, a quantity of pure linseed oil of the following analysis was secured:

Specific gravity at 15° C....................	0.934
Acid number	5
Saponification number	191½
Iodine number	188

This oil was distributed into a number of 8 oz. oil sample bottles, and to a series of these bottles was added varying quantities of a very concentrated drier made by boiling oil to 400° C. in an open kettle, with the subsequent addition of lead oxide. The amount of drier added to each bottle varied according to the percentage desired; being calculated on the lead content of the drier, which was very accurately determined by analysis.

There was secured in this manner a series of oils containing varying amounts of lead oxide, and from this lot was selected a certain number of samples which would be representative and typical of the vehicles of paints now found in the market.

Another series of tests were made by combining with a large number of samples of pure linseed oil as used above, various percentages of a manganese drier made by boiling oil at 400 degrees and incorporating therewith manganese dioxide.

Still another series of tests were made upon a number of oils into which were incorporated various small quantities of lead oxide and manganese oxide together, using the standard driers made in the above manner, all of which were carefully analyzed to determine their contents.

In view of the errors in manipulation that could occur where so many tests were made, it was not deemed advisable, in carrying out the tests, to use glass plates, on which only a minute quantity of oil could be maintained. A much better solution of the difficulty presented itself in using a series of small, round, crimped-edge tin plates about three inches in diameter, such as are used for lids of friction-top cans.

With paints it is impossible to secure films as thin as those presented by layers of oil on glass, nor would it be desirable to secure films of this same relative thickness. For this reason, an endeavor was made to conduct the following tests with films of the same relative thickness as that possessed by the average coating of paint. The drying of the films did not take place in the same short period, nor in the same ratio as with the thin layer that is secured by flowing oil upon glass. The results, however, are interesting.

The containers were carefully numbered in consecutive order.

corresponding to the numbers on the various samples of oil. A very small quantity of oil was placed in each of the covers, which were previously weighed, and allowed to distribute itself over the bottom surface thereof. Re-weighing of the covers gave the amount of oil which was taken for each test. The test samples in the covers were all placed in a large box with glass sides, having a series of perforated shelves. In the side of this box was an opening through which a tube was passed, carrying a continual current of air washed and dried in sulphuric acid. Oxidation of the oil films commenced at once, and the amount of oxygen absorbed was determined at suitable periods, by weighing, the increase in weight giving this factor. This test was kept up for a period of twenty days.

A test was also made in the same manner with a current of damp air passing into the box, to observe the relative oxidation under such conditions.

The results obtained are given in Tables 28-31.

The following outline will present to the mind of the reader the most salient points which have been gleaned from these experiments, and which should give the manufacturer some knowledge as to the percentage of oxides to use either in boiled oil, paints or varnishes.

In the case of lead oxide, an increase in the percentage added to the oil causes a relative increase in the oxygen absorption, but when a very large percentage of lead has been added, the film of oil dries to a film that is excessively hard.

In the case of manganese oxide, the increase in oxygen absorption on the first day is much more pronounced than is the case with lead oxides. Furthermore, the oxidation of manganese oils seems to be relative to the increase in manganese up to a certain period, when the reverse of this seems to take place, and beyond a certain definite percentage of manganese, added percentages seem to be of no value. The oxygen absorption with oils high in manganese has been noticed to be excessive, and the film of oil becomes surface-coated, drying beneath in a very slow manner, a condition that often leads to checking. The percentage where manganese renders the greatest efficiency seems to be 0.02 per

TABLE 28.

Linseed Oil and MnO_2 (Manganese) Drier—Test No. 1.

Per cent. MnO_2		0.02	0.05	0.15	0.25	0.35	0.45	0.55	0.70	1.00
Per cent. gain.......	1 day..	0.08	0.11	0.16	....	3.21	3.46	3.27	3.01	2.76
	2 days.	0.16	5.88	4.48	....	3.63	4.01	3.70	3.51	3.18
	3 days.	0.21	6.79	4.61	....	3.83	4.31	....	3.91	....
	4 days.	....	....	4.64	....	....	....	....	....	....
	5 days.	3.01	6.84	....	....	4.13	4.68	4.19	3.91	3.99
	6 days.	8.00	....	4.88	....	4.37	....	4.51	4.32	4.13
	7 days.	8.58	6.92	4.90	....	4.48	....	4.61	4.52	4.23
	8 days.	9.06	....	5.03	....	4.55	5.23	4.77	4.62	4.44
	9 days.	....	....	5.12	....	4.63	5.40	4.94	4.79	4.51
	10 days.	9.07	6.89	5.18	....	4.81	5.47	....	4.98	4.73
	11 days.	9.15	7.03	....	....	....	....	....	....	....
	12 days.	....	....	....	....	4.98	....	5.45	5.33	5.22
	13 days.	9.22	7.17	....	....	5.25	6.00	5.60	5.42	5.33
	14 days.	9.25	7.18	5.55	....	....	....	....	....	....
	20 days.	....	7.21	5.81	....	5.84	6.70	5.94	5.84	5.77

Above percentages of drier reckoned to metallic content.

TABLE 29.

Linseed Oil and MnO_2 (Manganese) Drier—Test No. 2 (Check).

Per cent. MnO_2		0.02	0.05	0.15	0.25	0.35	0.45	0.55	0.70	1.00
Per cent. gain........	1 day..	....	3.12	4.42	3.86	....	3.19	2.98	3.27	2.56
	2 days.	....	6.15	4.73	....	....	3.51	3.28	3.70	2.96
	3 days.	0.28	6.29	....	4.12	3.72	....	3.39	3.71	3.15
	4 days.	3.83	6.32	4.75	4.21	3.87	3.61	3.58	4.05	3.43
	5 days.	6.64	....	4.84	4.23	3.94	3.73	3.65	4.21	3.56
	6 days.	8.61	....	4.87	....	4.08	3.81	3.78	4.35	3.73
	7 days.	9.07	6.35	5.00	4.41	4.18	3.91	3.85	4.54	3.87
	9 days.	9.25	6.39	5.16	....	4.44	4.11	4.21	4.63	4.26
	11 days.	....	....	....	4.63	4.59	4.36	4.31	5.07	4.46
	16 days.	....	6.43	5.30	4.91	4.83	4.72	4.71	5.40	4.87

TABLE 30.

Linseed Oil and PbO (Lead) Drier.

Per cent. PbO		0.00	0.05	0.10	0.30	0.50	0.70	1.00	1.30	1.60	1.30	1.60
Per cent. gain	1 day..	0.042	0.049	0.092	0.058	0.066	0.062	0.062	0.079	0.039	0.14	0.72
	2 days.	0.098	0.104	0.153	0.116	0.158	.....	0.194	4.83	4.79	5.27	6.11
	3 days.	0.128	0.159	0.170	0.137	0.279	0.185	7.11	8.60	5.35	7.89	8.28
	4 days.	0.164	0.214	0.206	0.178	.....	4.07	7.39	9.55	8.53	7.93	8.68
	5 days.	0.176	.....	0.306	.....	0.340	7.60	7.47	9.87	8.78	8.18	....
	6 days.	0.188	0.231	.....	0.243	0.472	9.36	7.64	10.01	9.00	8.24	9.09
	7 days.	0.206	0.251	.....	0.253	1.080	10.06	....	10.14	....	....	....
	8 days.	0.212	0.253	.....	0.280	4.80	10.38	7.70	10.22	9.05	....	....
	9 days.	0.226	0.291	0.306	0.331	7.36	10.41	7.73	10.23	9.07	....	....
	13 days.	0.327	0.428	0.510	0.674	11.01	10.67	7.91	10.48	9.29	8.62	....
	15 days.	0.466	0.455	0.650	2.41	11.05	.....	7.92	10.50	9.30	....	....
	20 days.	0.521	1.08	1.78	8.76	11.25	10.67	7.98	10.52	9.36	....	....

TABLE 31.

Linseed Oil and PbO (Lead) and MnO_2 (Manganese)—Combination Drier.

Per cent. PbO		0.1	0.3	0.5	0.7	0.9	1.1	1.4
Per cent. MnO_2		0.005	0.015	0.025	0.35	0.45	0.55	0.7
Per cent. gain........	1 day.......	0.026	0.061	0.055	0.022	0.16	0.11	3.06
	2 days......	0.094	0.087	0.143	0.16	5.21	6.28	3.37
	3 days......	0.118	.....	0.17	4.23	7.63	8.31	3.74
	4 days......	.....	0.11	0.23	7.36	8.87	9.20	4.92
	5 days......	0.120	0.12	0.29	9.04	9.13	9.37	4.17
	6 days......	0.17	0.13	1.44	9.88	9.26	9.51	4.34
	7 days......	0.21	0.18	4.65	10.11	9.28	.....	4.45
	11 days......	0.30	0.26	10.03	10.35	9.61	9.85	5.11
	12 days......	.....	.....	.....	10.45	9.66	.....	....
	13 days......	0.35	0.54	10.37	10.51	9.67	10.03	5.33
	18 days......	0.49	3.43	10.38	10.62	9.68	.....	5.73

cent. This critical percentage, as it may be termed, should not be exceeded, as any added amount of manganese has the effect of making the film more brittle. In the same way with lead driers, excessive amounts of lead oxide seem to have no beneficial effect on the drying of an oil, and when the percentage which seems to be the most beneficial, namely 0.5 per cent. lead oxide, is exceeded, the film is apt to become brittle.

Oils containing lead oxide driers are less influenced in their drying tendencies by conditions of moisture in the atmosphere than oils containing manganese, but frequently, however, the former dry much better in a dry atmosphere. As a general rule, varnishes rich in manganese dry more quickly in a dry atmosphere, while those containing small quantities may in some instances dry more quickly in a damp atmosphere.

It was furthermore noticed in these tests that sulphuric acid, placed in dishes on the bottom of the large box in which the samples of oil were drying, were discolored and turned brown after several days, showing that the acid had taken up some material of a volatile nature that was a product of the oxidation.

Another curious feature of these tests was the development of a peculiar aromatic odor which was given off by the oils upon their drying in dry air. When the oils were dried in moist air, a rank odor resembling propionic acid was observed, and this led the observer to believe that a reaction was effected by the absorbed oxygen, that caused the glycerin combined with the linoleic acid as linolein to split up into evil-smelling compounds. It has been suggested that the oxygen first attacks the glycerin, transforming it into carbonic acid, water and other volatile compounds, which are eliminated before the oil is dried to linoxyn. Mulder has observed that in the process of linseed oil being oxidized, glycerin is set free, which becomes oxidized to formic, acetic and other acids, while the acid radicals are set free and are converted by oxygen into the anhydrides, from which they pass by further oxidation into linoxyn.*

The theory of auto-oxidation of linseed oil has been very ably treated by Blackler, whose experiments indicated that during the drying process the slow absorption of oxygen was, at a critical period, followed by a rapid absorption which he attributes to the presence of peroxides which accelerate oxidation. The materials produced by this peroxide formation may act as catalyzers and accelerate the formation of more peroxide. Lead and manganese oxides may also be oxidized to peroxides by the action of oxygen and in this event might act as very active catalyzing agents or carriers of oxygen. Blacker's statement that the presence of driers do not increase, but have a tendency to decrease the initial velocity of oxygen absorption, has been confirmed by these experiments.

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*See "The Composition of Paint Vapors," p. 218.

Some most interesting results were secured by dipping extremely fine copper gauze into linseed oil, and then suspending the gauze in the air. The adhesion of the oil to the copper caused the formation of films between the network, and remarkable drying action was observed. The copper or any superficial coating of copper oxide which may have been present on the metal, undoubtedly affected the result to some extent. It has been found that metallic lead is even more efficient than copper in this respect, but this may be due to the action of free acid in the linseed oil, forming lead linoleates, products that greatly accelerate drying. Another interesting experiment was made by taking pieces of gauze cloth and immersing in linseed oil. After the excess oil had been removed, by pressing, the cloth was again weighed to determine the amount of oil used for the experiment. The increase in oxygen absorption in this case was very rapid. In order to secure a more evenly distributed state of the oil, tests were conducted by saturating pieces of stiff blotting papers and after exposure weighing as usual.

The influence of light on the drying of oils is unquestionably a potent one. The practical painter knows that a certain varnish will dry quicker when exposed to the light than when in the dark. Chevreul was one of the first pioneers in this field of research to observe the effects of colored lights on drying, and he claimed that oil exposed under white glass dried more rapidly than when exposed under red glass which eliminates all light of short wave lengths.

Genthe obtained interesting results in the drying of oil submitted to the effect of the mercury lamp. Oxidation without driers was effected probably through the formation of peroxides. In commenting on this subject, Blackler* gives a description of the use of the Uviol Lamp, which is similar to the mercury lamp, but has instead of a glass casing, which cuts off the valuable rays, a fused quartz casing which allows their passage.

In the boiling of linseed oil, by certain processes the oil is slightly heated and manganese resinate is incorporated therein. It goes into solution quite rapidly. In other processes the oil is heated to 400 degrees or over, and manganese as an oxide is boiled into the oil. Although it is unsafe to say that a small percentage of rosin such as would be introduced by the use of resinate driers, is not harmful, yet this process should give a good drying oil, inasmuch as it has been found that no matter whether the manganese is added to the oil as a resinate, borate or oxide, practically the same drying effect is noticed in every case where the percentage of manganese is the same. It is the opinion of some, however, that the resinate driers are not as well suited for durability as oxide driers. However, if a boiled oil is found to contain on analysis a small percentage of rosin (less than 0.5 per cent.) it should not be suspected of adulteration. Practical tests, however, should be made with such oil along with an oil made with an oxide drier, before pronouncing on their relative values. Inasmuch as the addition of certain driers to linseed oil lessens the durability of the film, it is more practical to use the smallest amount of drier that will serve the purpose desired, that is, set the oil up in a paint to a hard condition which will not take dust and which will stand abrasion.

The results of this investigation would indicate that when lead or manganese linoleates are used, the most efficient results may be obtained with 0.5 per cent lead or with 0.05 per cent. manganese or with a combination of 0.5 per cent. lead and 0.02 per cent. manganese.

Until more definite results have been obtained with the *tungates* and cobalt salts, which will probably prove of exceptional interest as driers, the above driers will probably be used to the greatest extent.

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* M. B. Blackler: "The Use and Abuse of Driers," P. and V. Society. London. Sept. 9, 1909.

CHAPTER XXIII.

MISCELLANEOUS OIL INVESTIGATIONS.

Soya Bean Oil.—This oil, which has presented itself as a claimant for distinction in the list of paint oils, is now being imported into this country in large quantities. This oil is also produced in our own Southern States and is rapidly coming into the market for use in the manufacture of paints, soaps, and food products. It is obtained from the seeds of Soya Hispida, a plant indigenous to Manchuria, but raised extensively in America as a cattle food.

The writer has examined a number of representative samples of the oil that have come into this country, and the results obtained are shown in Table 32.

TABLE 32.

Chemical Characteristics of Soya Bean Oil.

Sample No.	Specific gravity.	Acid No.	Saponification No.	Iodine No.	Per cent of foots.
1	0.9233	1.87	188.4	127.8	3.81
2	0.9240	1.92	188.3	127.2	....
3	0.9231	1.90	187.8	131.7	....
4	0.9233	1.91	188.4	129.8	....
5	......	....	.....	130.0	....
6	......	....	.....	132.6	....
7	......	....	.....	136.0	....
Average.....	0.9234	1.90	188.2	130.7	....

It is evident that the iodine value of soya bean oil is the only chemical characteristic that markedly differentiates it from linseed oil. Therefore, in the detection of soya bean oil and its estimation, the iodine values of several samples of mixed oils are given, as being of interest in this connection (Table 33).

TABLE 33.

Iodine Values of Linseed Oil and Mixed Oils.

Sample No.	Straight linseed.	Soya. 25 per cent. Linseed. 75 per cent.	Soya, 50 per cent. Linseed, 50 per cent.	Soya, 75 per cent. Linseed. 25 per cent.
1	190.3	175.2	160.7	140.4
2	189.5	175.9	161.7	140.8
3	188.0	175.4	160.3	139.0
Average........	189.3	175.5	160.9	140.4

A series of tests were conducted to determine the rate of drying of soya oil treated with lead and manganese driers. A definite quantity of oil was placed in weighed friction-top can covers, which were re-weighed after receiving the oil, to determine the amount used for the test in each case. The tin covers containing the oil were then placed in a large box under definite temperature control and humidity, for a certain period. Weighings were made at different periods, and the increases in weight, due to absorption of oxygen, was calculated to percentages.

Table 34 gives the results obtained. The time of drying was somewhat longer than with linseed oil. Later tests show that driers prepared from cobalt resinate or linoleate are much more efficient than lead or manganese driers for drying soya oil.

TABLE 34.

Soya Bean Oil and Lead Drier.

Per cent PbO.		0.05	0.10	0.30	0.50	0.70	1.00	1.30	1.60
Per ct. gain..	1 day..	....	0.07	0.63	1.34	1.05	1.53	0.93	1.35
	3 days.	....	0.07	3.52	4.31	2.75	4.86	4.82	4.12
	5 days.	....	0.09	5.04	6.06	6.09	6.75	6.66	5.52
	12 days.	....	....	6.88	7.54	7.43	7.76	7.32	6.47
	15 days.	....	....	8.84	8.93	8.59	8.81	8.44	7.46
	20 days.	0.05	0.20	9.02	9.08	8.90	9.03	8.65	7.83

Soya Bean Oil and Manganese Drier.

Per cent MnO$_2$		0.01	0.05	0.15	0.26	0.30
Per ct. gain.....	1 day.....	....	....	0.02	0.02	0.01
	10 days....	....	5.06	6.48	6.10	5.97
	20 days....	0.05	9.07	8.80	6.78	6.51

Soya Bean Oil, Manganese and Lead Drier.

Per cent PbO.		0.20	0.30	0.50
Per cent MnO$_2$		0.05	0.15	0.25
Per ct. gain.......	1 day.....	3.04	3.77	3.74
	8 days....	5.96	6.43	6.47
	12 days....	6.33	6.78	6.67

The writer has found that a few drops of soya bean oil placed in a porcelain dish will give with a drop of strong sulphuric acid, faint fluorescent yellow and green colors, forming a pattern distinct from the dark-brown begonia-shaped leaf formed by sulphuric acid with pure linseed oil. Many other qualitative tests have been tried to detect the presence of soya oil in admixture with linseed oil. Soya oil seems, however, not to possess the chromogenetic properties of oils, such as cottonseed oil.

The writer recently submitted to a number of investigators on a sub-committee of Committee D-1, American Society for Testing Materials, several samples of commercial soya bean oils for examination and determination of their suitability for use in paints. The following directions were also submitted for guidance in the testing work:

Heat Test.—Heat 2 oz. of the oil at 450° F. in a glass receptacle until bleaching is noticed. Then blow a slow current of dry air through the oil until the specific gravity has increased to 0.950. This may require a period of 7 hrs. The blowing should be conducted at a temperature between 300° and 370° F. The oil should become light and fairly rapid drying.

Drying Test.—Place on a table a white sheet of paper 10 cm. square (100 sq. cm. in area). Upon this piece of paper place a weighed and marked piece of ordinary clear window glass about 15 cm. square. On the white area outlined on the paper below the glass, drop about 10 drops of the oil to be tested (approximately 200 mg.). Brush out the oil with a clean camel's-hair brush, so that it will cover the white area. Reweigh the glass to determine the amount of oil thereon. The plate may then be lifted by the edge which is uncoated and placed in a convenient place for drying. The number of hours required for the oil to dry to a firm film should be noted. The change in weight should be determined by reweighing the plate at the end of the third day.

In the determination of the analytical constants of soya oil, results which agree very closely were obtained by nearly all of the observers, which would indicate that soya oils have a fairly well-defined chemical constitution, even though they may be pressed from various seeds grown in different States. The average constants are given in Table 35.

TABLE 35.

Average Constants of Nine Samples of Raw Soya Bean Oil as taken from the Results of Nine Observers.

Specific gravity	0.9247
Saponification number	192.0
Iodine number	134.5
Acid number	2.14

The heat tests to which the soya oils were subjected gave interesting results, but did not in any case seem to increase the drying value of the oils. It is fairly well established by the tests however that most soya oils will bleach under the heat treatment.

In the drying tests, as a rule, rapid initial setting was observed with the blown oils, but they remained tacky for a long period of time. Unfortunately, the drying tests on the blown-oil samples gave widely varying results. Toch states that the abnormally high results obtained in his experiments were probably due to the deposition of extraneous matter on the films, the atmosphere where the tests were made being that of a manufacturing city. In another instance the operator flowed the oil upon the plates in thick films, rather than brushing the oil out as outlined in the instructions for the tests. The failure of the various members to obtain concordant results in these drying tests would indicate that the method used is not satisfactory in its present form. Nearly all observers noted a peculiar crawling of the films, which would indicate that raw soya oil is not well adapted to use as a paint oil, unless treated with a drier.

The charted results obtained by nine observers on two of the oils used in the tests are given below.

TABLE 36.

Soya Bean Oil No. 1.

Observer.	Sp. Gr. at 15°.5 C.	Saponification Number.	Iodine Number, Hanus.	Acid Number.	Heat Test Remarks.	Sp. Gr. Heated Oil.	Change in Weight of Heated Oil in 3 days, per cent.	Remarks.	Color Value.[1]
Gardner	0.9210	190.0	132.6	1.20	Same color; viscous.	0.926	1.20+		
Boughton	0.9248	197.4	134.1	2.50	Bleached	0.943	3.10+		10mm.
Lindsay	0.9248	190.2	133.7	1.21	Bleached well	0.959	6.86+		
Lawrie	0.9220	191.4	132.0	2.40	Bleached	0.937	1.10+		
Toch	0.9250	196.5	129.7	2.20	Good	....	10.00+		
Jackman & Stoppel	0.9248	192.4	132.2	2.24	Darkened	0.959	0.28+	Oil crawled on plate in drying test.	
Kohr & Mougey	0.9248	194.9	135.2	1.30	Same color	0.951	0.39+	Blown 12 hr.	
Pickard	0.9242	189.4	130.3	2.50	....	....	4.40+		
White & Boyle	0.9248	191.1	131.4	1.09	....	....	0.47+		
Average	0.9240	192.6	132.4	1.85	....	0.944	3.09+		

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[1] *Color.*—The color was compared with standard Lovibond glasses in a Schreiner colorimeter. A depth of 10 mm. of soya bean oil No. 1 was matched against a combination of glasses and used as a standard against which different depths of the other oils were matched.

TABLE 37.

Soya Bean Oil No. 2.

Observer.	Sp. Gr. at 15°.5 C.	Saponification Number.	Iodine Number. Hanus.	Acid Number	Heat Test Remarks.	Sp. Gr. Heated Oil.	Change in Weight of Heated Oil in 3 days, per cent.	Remarks.	Color Value.
Gardner	0.9210	190.0	135.2	2.50	Same color; viscous.	0.924	Lost		
Boughton	0.9251	196.3	135.3	2.10	Bleached slightly	0.941	0.10+		9 mm.
Lindsay	0.9246	188.3	134.2	2.29	Bleached	0.959	6.40+		
Lawrie	0.9210	194.4	132.4	1.90	Bleached	0.946	0.90+		
Toch	0.9250	191.0	130.5	2.10	Good	....	12.00+		
Jackman & Stoppel	0.9249	191.7	133.9	1.96	Darkened	0.952	0.12+	Oil crawled on plate in drying test.	
Kohr & Mougey	0.9257	189.0	137.3	2.30	Same color	0.950	0.19+	Blown 12 hr.	
Pickard	0.9246	185.6	133.8	2.20	....	.....	3.20+		
White & Boyle	0.9248	191.0	131.1	2.11	....	....	1.31+		
Average	0.9241	190.8	133.7	2.16	....	0.945	3.03+		

Perilla Oil.—A quantity of 300 pounds of perilla seed, the small round seed of *perilla nankinensis*, a plant grown extensively in China and Japan, was imported by the writer from Yokohama and received early in the fall of 1916. This seed will be used for experimental introduction in various parts of the country. A request has been made that the seed be sent out through the Bureau of Plant Industry and that sections of the country be selected where it is probable the seed will give the best results.

Another lot consisting of 666 pounds of seed (4 barrels) was submitted to the writer for crushing. Permission was obtained from the Department of Agriculture to use their half-size commercial oil press. The seed was fed in at one end and carried by screw to the pressure die, where the oil was expelled, leaving the press cake. Nearly 25 gallons of oil were obtained. It was of fairly light color and clear. It will be distributed for coöperative investigation to members of the Committee on Testing Paint Vehicles of the American Society for Testing Materials. The following data was obtained on the four-barrel crushing test:

Analysis of Perilla Seed.

Oil in seed (ex.)	33.73%
Cake residue	66.27%

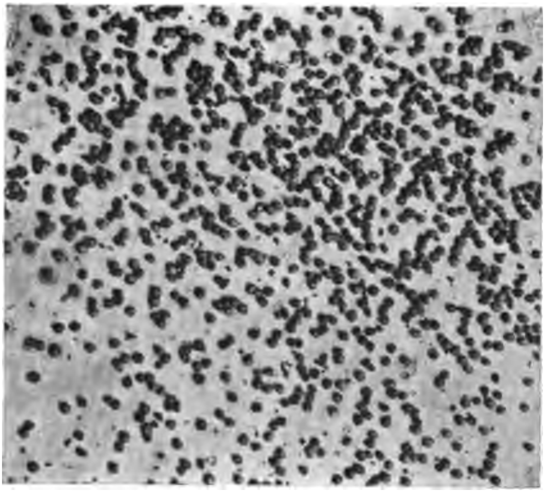

FIG. 137.
Perilla Seed.

Analysis of Perilla Press Cake.

The press cake from the seed was thoroughly extracted with benzine and the cake dried and examined. The following results were obtained:

Nitrogen	5.28%
Phosphoric anhydrid	2.58%
Soda (Na_2O)	.56%
Potash (K_2O)	1.50%

Analysis of Perilla Oil.

Specific gravity	.937
Acid No	4.3
Iodine No	193.3
Saponification No	193.4
Refractive index	1.4780

Tests on Perilla Oil.—The work carried out during 1916 by the sub-committee on testing paint vehicles, of the American Society for Testing Materials, was entirely devoted to a study of the oil derived from the perilla plant, which has probably the highest iodine number of any known drying oil obtainable in commercial quantities. The oil was pressed from a ton of perilla seed that was purchased by the Educational Bureau of the Paint Manufacturer's Association of the United States from a New York broker and importer. Portions of the seed were distributed to experimenters in various states throughout the country, to determine in what climates it could best be grown. The seed was old and did not germinate properly, so the growing tests were discontinued. The remainder of the seed was turned over to the U. S. Department of Agriculture for crushing tests.

The following information concerning the expression of the oil is of interest:

Perilla seed, absolute ether extract	44.35
Perilla seed cake, absolute ether extract	14.65
Weight of seeds pressed, lbs	485
Oil obtained, gallons	about 18

The writer's experiments with this oil are shown below:

Constants of Perrila Oil as Received.—The constants of the oil as received were as follows:

Specific gravity	0.935
Acid number	7.2
Saponification number	194.2
Iodine number	198.3

Investigation of Effect of Heat Treatment upon Constants.—Several portions of the oil were heated individually in open beakers to 300, 400 and 500° F., respectively, the oil samples being held at these temperatures for a period of ten minutes. Upon cooling, the samples were examined and their constants determined. These are as follows:

Specific gravity	0.935	0.936	0.936
Acid number	7.6	6.5	6.6
Saponification number	193.8	193.2	194.0
Iodine number	198.2	195.5	189.1

Experiments on the Drying Properties of Perilla Oil in Paints.—To determine the relative drying properties of linseed oil and perilla oil, samples of sublimed white lead, zinc oxide, and lithopone were individually ground in perilla oil and in linseed oil. The proportion of pigment to oil in each case was standard, the amounts being as follows:

Sublimed white lead..	Pigment 70 per cent, Oil 30 per cent
Zinc oxide	Pigment 50 per cent, Oil 50 per cent
Lithopone	Pigment 60 per cent, Oil 40 per cent

During grinding, it was apparent that perilla oil forms a paint of greater body than linseed oil.

Without the addition of drier or thinner of any type, these paints were spread upon wooden surfaces and the drying times noted. They are as follows:

	In Linseed Oil.	In Perilla Oil.
Sublimed white lead...........	17 hours	17 hours
Zinc oxide	17 hours	20 hours
Lithopone	17 hours	20 hours

All the paints in the above tests were then treated with 2 per cent of a concentrated liquid drier. They were again brushed out upon wooden surfaces and the time of drying in each case was substantially 12 hours, the perilla-oil paints showing somewhat greater hardness of film.

These tests indicate that although perilla oil has a higher iodine number than linseed oil, it is not necessarily a better drying oil when used in its raw state. Nevertheless, it is apparent that the addition of drier to the perilla oil rapidly accelerates its oxygen-absorbing properties, possibly to a greater extent than would be shown by a linseed oil of equal iodine value.

Exposure tests made by the writer on large-size wooden panels painted with a mixture of white lead and zinc pigments ground in linseed oil and mixtures of linseed oil with varying percentages of perilla oil, have now been exposed for over six years, repainting tests having been made two years ago.* These tests show that perilla oil forms a very durable paint, the results obtained with many of the mixtures being equal to or possibly superior to those shown by straight linseed oil.

Experiments on the Suitability of Perilla Oil for Use in Linoleum Manufacture.—In the manufacture of linoleum, two types of oxidized oil are used. For the production of rolled linoleum, linseed oil is raised to a temperature of 400° F., there being added during the heating, litharge and red lead as drier, in the proportion of about 1 per cent. The oil is then blown with a current of air for about two hours. This oil is subsequently transferred to so-called oxidizing kettles where it is raised to a temperature of about 600° F. At this point the oil is blown for a period of about 3 hours. It is then poured into a box and allowed to cool to a rubber-like solid which is cut up into large chunks approximately the size of hams. These are sprinkled with red lead, ochre and similar pigments and put through steam-heated rolls where the mass is rolled on a fabric backing.

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* H. A. Gardner, "The Practical Testing of Drying and Semi-Drying Paint Oils," Proceedings, Am. Soc. Test. Mats., Vol. XI, p. 641 (1911).

For the production of inlay linoleum, linseed oil is allowed to flow over large sheets of scrim cloth hung from the ceiling of a so-called scrim house. The alternate flooding and oxidation produces at the end of several months a sheet of oxidized oil approximately ½ in. in thickness. Upon aging, this is ground up, being very friable, and a meal of oxidized oil results. This is mixed with wood flour, color and binder and pressed into molds to form the desired pattern.

The writer has experimented with perilla oil and has found that it may be used with excellent results for the manufacture of either type of oxidized oil referred to above. The tests made were on a laboratory scale, but followed in detail the commercial practice of preparing the solidified oil produced from linseed.

Perilla-Oil Cloth Varnish.—The writer has also used perilla oil successfully in varnish, and at his suggestion over 100 barrels of the oil was used in some experimental batches of varnish that was used for table-oil cloth with even more successful results than the tung oil that had previously been used.

Lumbang Oil.—This oil is obtained from the fruit of a tree known as *aleurites moluccana,* indigenous to Polynesia and now widely cultivated in certain parts of Asia as well as in tropical islands—Hawaii and the Philippines. Experiments have shown that the tree also flourishes on the Florida peninsula and certain parts of the Gulf coast. It is of the same family as the tung tree, and the oil closely resembles tung oil in analytical constants, but does not have the peculiar properties of polymerization shown by the latter. Its constitution is, moreover, different from that of tung oil. The tree is a highly ornamental shade tree, growing to a height of thirty or forty feet, widely spreading its branches and producing large, glossy leaves. It bears two heavy crops of fruit, which contain the so-called lumbang nuts. These consist of heavy shells containing a light-colored kernel or meat rich in oil. The kernels burn freely with a sooty flame, and are often used as a source of illumination by the natives, thus acquiring the local name of candle nuts. The nuts have a pleasant taste, resembling Brazil nuts. The oil from the nuts is almost colorless and has a purgative action. This would indicate that the oil might find a use in medicine, and would suggest further experiments.

When the nuts are pressed for the oil content, a press cake is left which is highly prized by the natives for its fertilizing action, a price of $100 a ton being paid for it in preference to ground fish or tankage at $25. The natives apparently are successful in producing a most remarkable stimulus of growth in certain plants through its use. The chemical analysis of the press cake produced in the writer's experiments showed a very considerable amount of valuable plant foods, which probably are in a readily assimilable form. With the oil marketing in Manila at 60 cents a gallon and being used there in the crude manufacture of soap, painting of river craft, etc., it is probable that considerable quantities could be obtained for export, if desired.

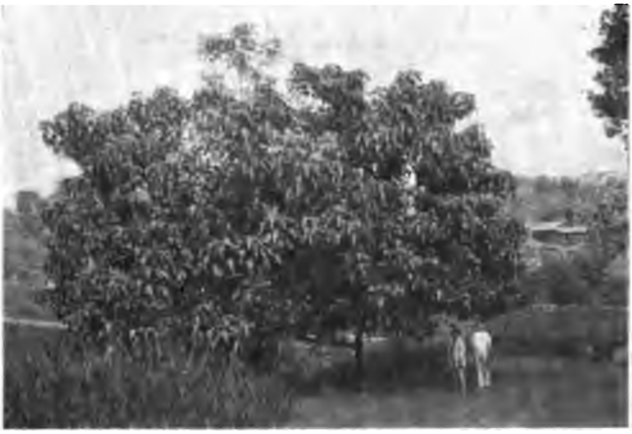

FIG. 138.

Lumbang Tree.

NOTE.—Acknowledgment is made to Dr. David Fairchild of the Bureau of Plant Industry for much of the information regarding the lumbang tree as well as for two of the photographs which appear.

The difficulty in obtaining very large amounts of the oil lies in the present unsatisfactory method of getting the kernels out of the shells. This work is done by the natives in a very crude way, the seeds being crushed by hand on rocks and the meats cut out with knives, since they adhere tenaciously to the sides of the shells. Working on a shipment of 576 pounds of the nuts imported from Hawaii, the writer proceeded as follows: The nuts were first passed through a Chipmunk crusher, breaking them into small pieces. They were then screened in order to separate the larger pieces of meat. Five boys were then employed for a period of five days in picking out the small particles of meats left in the shells. A portion of the meats or kernels was then cold pressed, after they were placed in a canvas bag suspended in an apparatus made of a number of rigid iron slats banded together and welded into a plate base. Into this apparatus was inserted a metal plunger attached to a testing machine. A practically colorless oil was obtained. Before pressing the balance of the seed it was thought desirable to remove the small pieces of cracked shell remaining in the meats. A flotation method was developed, which it was thought might prove practicable for the rapid and complete separation of the meats from the cracked shells, as

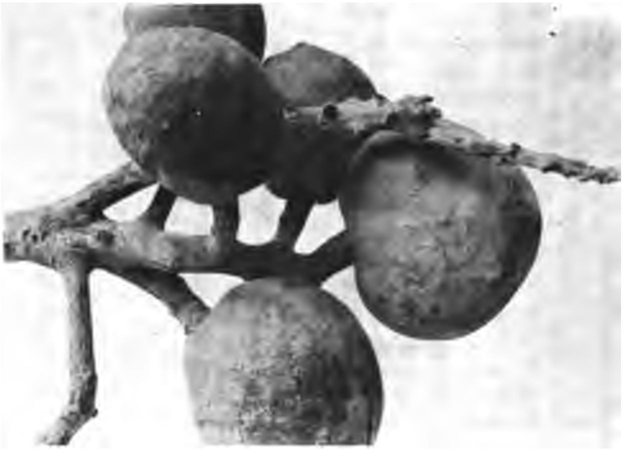

FIG. 139.
Fruit of the Lumbang Tree.

the broken nuts were delivered from the crusher. The mixture of meats and shells were, therefore, placed, in successive quantities, in a tub of water in which there was dissolved 5 per cent of table salt to increase its gravity. The cracked shells fell to the bottom and the oily meats floated on the surface of the salt solution, being removed and dried. The separation was rapid and complete. Unfortunately, however, the meats absorbed a considerable amount of the salt solution and during drying partial hydrolysis of the oil in the meats occurred.

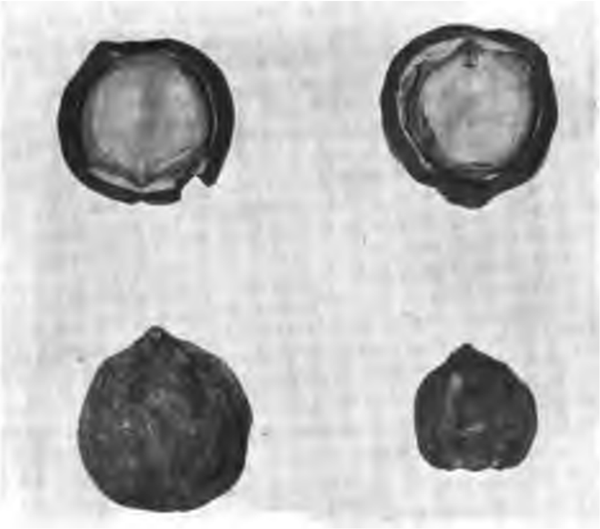

FIG. 140.

Upper views are of a Lumbang Nut cracked open. Lower view on left is of a Lumbang Nut as obtained from the fruit. Lower right is of the kernel from a Lumbang Nut. Views are about two-thirds actual size of nuts.

Moreover, the water acted as an extractive upon the cracked shells and took into solution a large amount of a brown, tannin-like dye that discolored the oil in the seed. When the dried meat was pressed, the oil obtained was therefore dark in color and had a very high acid number. The several gallons obtained will be used in the preparation of the fatty acids of lumbang oil, and a study of these acids should give some interesting data.

Data on the pressing of the lumbang nuts and analysis of the cake are appended.

Analysis of Lumbang Nuts.

Average weight of nut	11.7 grams
Percentage of shells	67.9%
Percentage of kernels or meat	32.1%
Percentage of oil in shells (ex.)	0.6%
Percentage of oil in kernels (ex.)	60.3%
Ash of kernel	3.2%
Nitrogen in kernel	3.2%

Analysis of Lumbang Press Cake.

The press cake from cold pressing was thoroughly extracted with benzine to remove any oil present and then dried. The dried press cake had the following values:

Nitrogen	7.34%
Phosphoric anhydrid	3.95%
Soda (Na_2O)	0.47%
Potash (K_2O)	1.42%

Analysis of Cold Pressed Lumbang Oil.

Specific gravity	.927
Acid No	1.3
Iodine No	162.0
Saponification No	192.3
Refractive index	1.475

Tung Oil.—During the years 1911-1916, the writer and members of a sub-committee of Committee D-1, American Society for Testing Materials, examined a large number of samples of Chinese wood oil.* A brief summary of some of the results obtained in this work is outlined below. The first table gives the data obtained from pressing a quantity of tung nuts obtained from China and identified by the Bureau of Plant Industry of the U. S. Department of Agriculture as *Aleurites fordii.*

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*For complete reports see Proceedings A. S. T. M.

Average weight of nut, g	2.4
Shells (determined on 5.78 kg. of nut), per cent	41.6
Kernels by difference, per cent	58.4
Moisture in kernels (loss in CO_2 at 100° C.), per cent	2.6
Ash, per cent	2.2
Nitrogen, per cent	2.44
Ether extract, per cent	64.1
Ether extract from shells, per cent	1.0
Ether extract of press cake, per cent	7.2

The oil had the following constants:

Specific gravity	.939
Refractive index	1.521
Acid No	.9
Saponification No	191.
Iodine No	169.5
Heat test (minutes)	8.75

Another quantity of Chinese wood oil, crushed from two lots of nuts procured in Leon County, Florida, and representing the 1914 crop, was pressed by Dr. Bailey of the Bureau of Chemistry, U. S. Department of Agriculture. The following data were obtained:

	Lot No. 3.	Lot No. 4.
Average weight of nuts, g	18.4	19.5
Percentage of kernel by weight of nuts	46.0	35.0
Loss of kernel in CO_2 at 100° C., per cent	3.18	2.43
Ash of kernel, per cent	2.50	2.30
Total nitrogen in kernel, per cent	2.60	2.54
Ether extract, per cent	64.18	65.00

Analysis of these oils gave the following results:

TABLE 38.

Summary of Results on Chinese Wood Oils (American).

Observer.	Iodine Jelly Test, minutes and seconds.		Heating Test (Browne's Method), minutes and seconds.		Iodine Number (Hübl, 17 hr.)		Saponification Number.		Acid Number.	
	Oil No. 3	Oil No. 4	Oil No. 3	Oil No. 4	Oil No. 3	Oil No 4	Oil No. 3	Oil No. 4	Oil No. 3	Oil No. 4
Gardner and Carmick	2-45	2-45	10-0	9-30	167.4	168.5	190.0	189.6	0.9	0.6

Examination of Special Tung Oils.—Three samples of oil were also examined by individual committee members. These samples were crushed from American-grown nuts. Samples

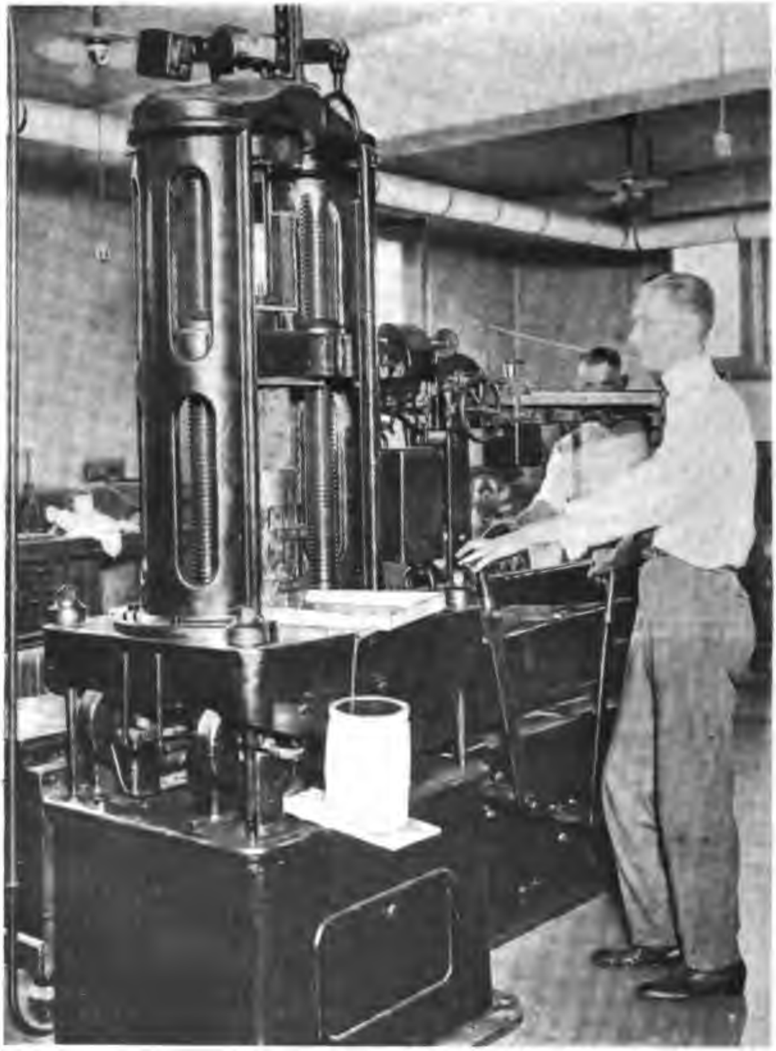

FIG. 141.

Crushing Lumbang Kernels in Laboratory Press.

Nos. 1 and 2 represented oils obtained from first-crop nuts produced from tung-oil trees planted in Tallahassee, Fla. The following data were obtained at the time of expressing Sample No. 1 from the nuts:

Average weight of nuts, g	3.3
Kernels, per cent	58.2
Loss of kernels in CO_2 at 100° C., per cent	2.41
Ash of kernel, per cent	2.47
Total nitrogen in kernel, per cent	2.05
Ether extract, per cent	68.0

The weight of the nuts received was 14.5 pounds. The hulls were separated from the kernels pressed without previous treatment, in an Anderson Expeller. The thick dark oil from the press contained a large quantity of finely divided press cake and was filtered on a Buchner funnel.

The following data were obtained at the time of expressing Sample No. 2 from the nuts:

Analysis of Kernel.—63.5 per cent of kernel in whole nut; 1.08 per cent of moisture in kernel; 66.90 per cent of ether extract in kernel.

Yield of Oil.—By extraction, 765 g. oil from 1710 g. of kernel = 44.73 per cent; by expression, 632.7 g. oil from 1710 g. of kernel = 37.00 per cent.

The oil produced was of very light color—in fact, almost as light as commercial castor oil—and had a rather pleasant but characteristic tung-oil odor. On account of the fact that the oil was almost neutral, the odor was not as pronounced as that given off by commercial tung oil that has a high acid number.

The oil obtained from the nuts gave the following constants:

TABLE 39.

Constants of American-grown Tung Oils.

Sample No.	Observers.	Appearance.	Odor.	Refractive Index at 25° C.	Specific Gravity at 15°.5/15°.5 C.	Acid Number.	Saponification Number.	Iodine Number (Hübl, 18 hours.	Iodine-Jelly Test, minutes.	Heating Test (Browne's Method), minutes.	Titer of Fatty Acids, deg. Cent.
1	Gardner and Carmick	Clear when received. Became cloudy over night.[a]	Neutral	1.5210	0.9390	0.8	192.6	170.8	8.0	10.5	......
1	Boughton	Light yellow. Very light turbidity.	Very slight. Becomes pronounced on standing.	....	0.9416	0.2	192.1	171.7	2.5	11.5	......
2	Gardner and Carmick	Very light color.[b]	Neutral	1.5200	....	0.4	190.2	165.9	8.0	10.0	......
2	Boughton	White, waxy, solid.	Very slight.	....	....	0.4	192.4	165.3	3.0	11.5	59.1

[a] Became white granular solid in two days.

[b] Oil was partially crystallized when received; later it became solid throughout. Probably due to a polymerization by light. Heating to 35° C. restores oil to a clear, normal condition.

[c] At 15°/15° C.

Standard Specifications for Purity of Raw Chinese Wood Oil (Tung Oil).

American Society for Testing Materials (1915).

I. PROPERTIES AND TESTS.

1. Raw Chinese wood oil shall conform to the following requirements:

PROPERTIES.

	Maximum.	Minimum.
Specific Gravity at $\frac{15°.5}{15°.5}$ C.	0.943	0.939
Acid Number	6	.....
Saponification Number	195	190
Unsaponifiable Matter, per cent	0.75	.....
Refractive Index at 25° C.	1.520	1.515
Iodine Number (Hübl, 18 hours)	.....	165
Heating Test (Browne's Method), minutes	12	.....
Iodine Jelly Test, minutes	4	.....

II. METHODS OF TESTING.

2. The recommended methods of testing are as follows:

Specific Gravity.—Use a pyknometer accurately standardized and having a capacity of at least 25 cc., or any other equally accurate method, making the test at 15°.5 C., water being 1 at 15°.5 C.

Acid Number.—Weigh 10 g. of oil in a 200-cc. Erlenmeyer flask, add 50 cc. of neutral alcohol, connect with a reflux air condenser (or place small funnel in neck of flask), and heat on a steam bath for ½ hour. Remove from the bath, cool, add phenolphthalein, and titrate the free acid with N/5 sodium hydroxide. Calculate as the acid number (milligrams of potassium hydroxide to 1 g. oil).

Saponification Number.—Weigh from 2 to 3 g. of oil in a 200-cc. Erlenmeyer flask, add 30 cc. of a N/2 alcoholic solution of potassium hydroxide, connect with a reflux condenser, heat on a steam bath for 1 hour, then titrate with N/2 sulphuric acid, using phenolphthalein as indicator. Always run two blanks with the alcoholic potash. From the difference between the number of cubic centimeters of acid required by the blanks and the determinations, calculate the saponification number (milligrams of potassium hydroxide to 1 g. of oil).

Unsaponifiable Matter.—To 25 g. of oil add 15 cc. of an aqueous solution of KOH (200 g. of KOH dissolved in water and made up to 300 cc.) and 35 cc. of 95-per-cent alcohol. Connect with a reflux condenser and heat on the water bath for 1 hour with occasional shaking. Transfer to a separatory funnel containing a little water and wash out flask with water, using in all 125 cc. Cool, add 200 cc. of ether and shake vigorously for 1 minute. In a few minutes the ether solution will separate perfectly clear. Draw off the soap solution into another separatory funnel. Shake the soap solution with three 100-cc. portions of ether. Unite all the ether portions and wash with three 30-cc. portions of water. Filter the ether solution (small portions at a time) into a tared flask, distill off the ether and dry flask and contents to constant weight at 95 to 100° C. in a steam oven. Report the percentage of unsaponifiable matter.

Refractive Index.—Use a properly standardized Abbé refractometer at 25° C., or any other equally accurate instrument.

Iodine Number (Hübl).—Place a small quantity of oil into a small weighing bottle or beaker. Weigh carefully. Transfer by dropping from 0.2 to 0.3 g. to a 500-cc. bottle having a well-ground stopper, or a specially flanged neck, iodine-test Erlenmeyer flask. Reweigh the weighing bottle or beaker to determine the amount of oil used in the test. Then dissolve the oil in 10 cc. of chloroform and add an amount of Hübl solution containing twice the amount of iodine that will be absorbed by the oil. Stopper the flask, shake well, and place in a dark closet for 18 hours. Add 20 cc. of a 10-per-cent solution of potassium iodide and 100 cc. of distilled water. Titrate with N/10 sodium thiosulphate, using starch as an indicator. Blank tests must be made. From the difference between the amounts of sodium thiosulphate required by the blanks and the determination, calculate the iodine number (centigrams of iodine to 1 g. of oil).

On account of the fact that Hübl solution after preparation is apt to deteriorate in strength, it is considered advisable to have prepared the two component parts of Hübl solution, namely, a solution of mercuric chloride in alcohol and a solution of iodine in alcohol, of the proper strength, as outlined in text-books. The proper amounts of these solutions may be mixed on the day of use.

Heating test (Browne's Method).—Test tubes for containing the oil should be 16 cm. by 15 mm., with a mark near the bottom to indicate 5 cc., and closed by a cork so perforated that a glass rod 3 mm. in diameter could move freely.

Fill a copper beaker (height, 12 cm.; internal diameter, 6 cm.) with cottonseed oil to a height of 7.5 cm. Place a thermometer so as to be 1.5 cm. from the bottom of the bath.

Use a nitrogen-filled, immersed-stem chemical thermometer, engraved stem; total length 4 to 4½ in.; graduated from 210 to 310° C. in 2° intervals; the length between 210 and 310° C. not less than 2½ in. If preferred, use emergent-stem thermometer 30 cm. long, with graduations from 100 to 400°

C., making correction for emergent stem according to the method outlined in Stem Correction Sheet No. 44 of the U. S. Bureau of Standards.

When the bath temperature is 293° C. (560° F.) and very slowly rising at this point, place the tube containing 5 cc. of the oil to be tested so that its bottom is level with the lowest part of the bulb of the thermometer. Note the time, remove the source of heat for about 45 seconds and then reapply. Before 2 minutes have elapsed the temperature of the bath will have fallen to 282° C. (540° F.), at which point it should be kept as steady as possible. When the wood oil has been in the bath about 9 minutes, raise the glass rod at intervals of 1/2 minute, and when the rod is firmly set note the time. As setting or jellying takes place within a few seconds of fluidity, a good end determination is afforded. Remove the specimen at once, heat the bath again to 293° C., and repeat the experiment with another portion of the sample.

No stirrer is used in the bath. A screen around the bath enables the temperature to be more easily reached. When the cottonseed oil has become tarry and viscid, it should be renewed; otherwise heating may be irregular.

Iodine Jelly Test.—In a wide-necked 200-cc. Erlenmeyer flask, place 2.5 g. (weight correct to 1 mg.) of the oil. Add 10 cc. of chloroform from a pipette and stopper the flask immediately. Carefully insert a small glass vial into the flask so that the vial stands upright. Into the vial from a pipette run 10 cc. of a solution of iodine in chloroform, containing 0.035 to 0.036 g. of iodine per cubic centimeter. Place the flask in a bath containing water at 25 to 26° C. and allow it to stand there for a few minutes. Keep the flask stoppered, except when it is necessary to remove it to insert the vial and to add the iodine solution. Tilt and rotate the flask so that the vial is upset and the contents of the flask are thoroughly mixed, at the same time starting a stop watch. Keep the flask in the bath at 25 to 26° C. and at the end of every quarter minute, tilt the flask towards a horizontal position. Note the time required for the formation of a jelly that does not flow, but sticks to the bottom of the flask or slides as a mass. Record time in minutes and quarters thereof. Pure Chinese wood oil should require 2¾ to 3¼ minutes for the formation of the jelly. If the temperature of the laboratory is more than 2 or 3° C. above or below 25° C., place the flask containing the iodine solution in the bath and allow it to remain there for several minutes before pipetting out the 10 cc. for the test. The arrangement of the apparatus is shown in Fig. 142.

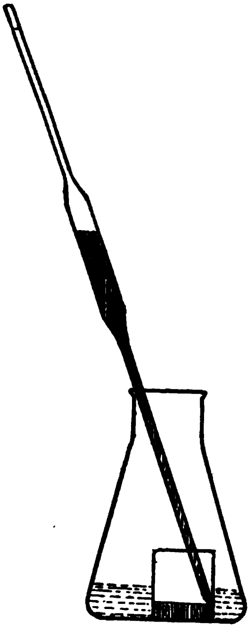
FIG. 142.

The chloroform used to dissolve the oil and to prepare the iodine solution shall conform to the requirements of the United States Pharmacopœia and shall have a specific gravity at 25°/25° C. of not more than 1.481 and not less than 1.480. The proper density can be obtained by washing with water if the specific gravity is too low or by adding 95-per-cent ethyl alcohol if too high.

A convenient procedure for preparing the iodine solution is as follows: Treat an excess of iodine with warm chloroform and after shaking for a few minutes, cool the contents to about 20° C. and filter through glass wool. Pipette 10 cc. of the solution into a flask containing 10 cc. of 10-per-cent potassium-iodide solution and titrate with 0.1 normal sodium-thiosulphate solution. Calculate the iodine content and dilute with chloroform so as to obtain an iodine content of 0.035 to 0.036 g. per cc. After dilution, titrate again against the thiosulphate to be sure that the solution is of required strength.

All the details of the above method must be followed exactly.

Standard Specifications for the Purity of Raw Linseed Oil from North American Seed.

American Society for Testing Materials (1913).

PROPERTIES AND TESTS.

Raw linseed oil from North American seed shall conform to the following requirements:

PROPERTIES.	Maximum.	Minimum.
Specific Gravity at $\frac{15^\circ.5}{15^\circ.5}$ C.	0.936	0.932
or		
Specific Gravity at $\frac{25^\circ}{25^\circ}$ C.	0.931	0.927
Acid Number	6.00	.....
Saponification Number	195	189
Unsaponifiable Matter, per cent	1.50	.....
Refractive Index at 25° C.	1.4805	1.4790
Iodine Number (Hanus)	.....	.178

METHODS OF TESTING.

The recommended methods of testing are as follows:

General.—All tests are to be made on oil which has been filtered at a temperature of between 60° and 80° F. through paper in the laboratory immediately before weighing out. The sample should be thoroughly agitated before the removal of a portion for filtration or analysis.

Specific Gravity.—Use a pyknometer, accurately standardized and having a capacity of at least 25 cc., or any other equally accurate method, making a test at 15.5° C., water being 1 at 15.5° C., or a test at 25° C., water being 1 at 25° C.

Acid Number.—Expressed in milligrams of KOH per gram of oil. Follow the method described in Bulletin 107, revised 1908, Department of Agriculture, Bureau of Chemistry, page 142. (See Appendix A.)

Saponification Number.—Expressed as with Acid Number. Blanks should also be run to cover effect of alkali in glass. Follow method given in Bulletin 107, revised 1908, Department of Agriculture, Bureau of Chemistry, pages 137-138. (See Appendix B.)

Unsaponifiable Matter.—Follow Boemer's method taken from his Ubbelohde Handbuch Der Öle u. Fette, pages 261-262. "To 100 g. of oil in a 1000 to 1500-cc. Erlenmeyer flask add 60 cc. of an aqueous solution of potassium hydroxide (200 g. KOH dissolved in water and made up to 300 cc.) and 140 cc. of 95 per cent. alcohol. Connect with a reflux condenser and heat on the water bath, shaking at first until the liquid becomes clear. Then heat for one hour with occasional shaking. Transfer while yet warm to a 2000-cc. separatory funnel to which some water has been added; wash out the Erlenmeyer with water, using in all 600 cc. Cool, add 800 cc. of ether and shake vigorously one minute. In a few minutes the ether solution separates perfectly clear. Draw off the soap, filter the ether (to remove last traces of soap) into a large Erlenmeyer, and distill off the ether, adding if necessary one or two pieces of pumice stone. Shake the soap solution three times with 400 cc. of ether, which add to the first ether extract. To the residue left after distilling the ether add 3 cc. of the above KOH solution, and 7 cc. of the 95 per cent. alcohol, and heat under reflux condenser for 10 minutes on the water bath. Transfer to a small separatory funnel, using 20 to 30 cc. of water, and after cooling shake out with two portions of 100 cc. of ether; wash the ether three times with 10 cc. of water. After drawing off the last of the water, filter the ethereal solution so as to remove the last drops of water, distill off the ether, dry residue in water oven and weigh."

Refractive Index.—Use a properly standardized Abbé Refractometer at 25° C., or any other equally accurate instrument.

Iodine Number (Hanus).—Follow the Hanus method as described in Bulletin 107, Revised 1908, Department of Agriculture, Bureau of Chemistry, page 136. (See Appendix C.)

APPENDIX.

METHODS OF TESTING REFERRED TO IN SPECIFICATIONS.

For the convenience of those who may not have a copy of Bureau of Chemistry Bulletin No. 107, the paragraphs referred to are here quoted. (Copies of the Bulletin may be obtained from the Superintendent of Documents, Washington, D. C., at 20 cents each.)

A.—Free Fatty Acids.—Provisional.

Weigh 20 grams of fat or oil into a flask, add 50 cc. of 95 per cent. alcohol which has been neutralized with weak caustic soda, using phenolphthalein as indicator, and heat to the boiling point. Agitate the flask thoroughly in order to dissolve the free fatty acid as completely as possible. Titrate with tenth-normal alkali, agitating thoroughly until the pink color persists after vigorous shaking.

Express results either as percentage of oleic acid, as acid degree (cubic centimeters of noral alkali required to neutralize the free acids in 100 grams of oil or fat), or as acid value (milligrams of potassium hydroxide required to saturate the free acids in 1 gram of fat or oil).

1 cc. of tenth-normal alkali = 0.0282 gram of oleic acid.

B.—Saponification Number or Koettstorfer Number.—Official.

(a) PREPARATION OF REAGENTS.

(1) Standard sodium hydroxide solution.—Use a tenth-normal solution of sodium hydroxide. Each cubic centimeter contains 0.0040 gram of sodium hydroxide and neutralizes 0.0088 gram of butyric acid.

(2) Alcoholic potash solution.—Dissolve 40 grams of chemically pure potassium hydroxide in 1 liter of 95 per cent. redistilled alcohol.* The solution must be clear and the potassium hydroxide free from carbonates.

(3) Standard acid solution.—Prepare accurately a half-normal solution of hydrochloric acid.

(4) Indicator.—Dissolve 1 gram of phenolphthalein in 100 cc. of 95 per cent. alcohol.

(b) DETERMINATION.

Conduct the saponification in a wide-mouth Erlenmeyer flask holding from 250 to 300 cc. Clean thoroughly by washing with water, alcohol, and ether, wipe perfectly dry on the outside and heat for one hour at the temperature of boiling water; allow to cool and weigh.

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*The alcohol should be redistilled from potassium hydroxide on which it has been standing for some time, or with which it has been boiled for some time, using a reflux condenser.

Run in about 5 grams of the filtered melted fat by means of a pipette, and after cooling again weigh the flask and contents. Pipette 50 cc. of the alcoholic potash solution into a flask by allowing it to drain for a definite time. Connect the flask with a reflux condenser and boil for 30 minutes or until the fat is completely saponified. Cool and titrate with half-normal hydrochloric acid using phenolphthalein as indicator. The Koettstorfer number (milligrams of potassium hydroxide required to saponify 1 gram of fat) is obtained as follows: Subtract the number of cubic centimeters of hydrochloric acid used to neutralize the excess of alkali after saponification from the number of cubic centimeters necessary to neutralize the 50 cc. of alkali added; multiply the result by 28.06 (the number of milligrams of potassium hydroxide per cubic centimeter) and divide by the number of grams of fat used. Conduct two or three blank experiments, using the same pipette and draining for the same length of time.

C.—Iodine Absorption Number.—Official.

(a) PREPARATION OF REAGENTS.

(1) Hübl's iodine solution.—Dissolve 26 grams of pure iodine in 500 cc. of 95 per cent. alcohol. Dissolve 30 grams of mercuric chloride in 500 cc. of 95 per cent. alcohol. Filter the latter solution, if necessary, and mix the two solutions. Let the mixed solution stand twelve hours before using.

(2) Hanus iodine solution.—Dissolve 13.2 grams of iodine in 1,000 cc. of glacial acetic acid (99.5 per cent.) showing no reduction with bichromate and sulphuric acid; add enough bromine to double the halogen content determined by titration—3 cc. of bromine is about the proper amount. The iodine may be dissolved by the aid of heat, but the solution should be cold when bromine is added.

(3) Decinormal sodium thiosulphate solution.—Dissolve 24.8 grams of chemically pure sodium thiosulphate, freshly pulverized as finely as possible and dried between filter or blotting paper, and dilute with water to 1 liter at the temperature at which the titrations are to be made.

(4) Starch paste.—Boil 1 gram of starch in 200 cc. of distilled water for ten minutes and cool to room temperature.

(5) Solution of potassium iodide.—Dissolve 150 grams of potassium iodide in water and make up 1 liter.

(6) Decinormal potassium bichromate.—Dissolve 4.9083 grams of chemically pure potassium bichromate in distilled water and make the volume up to 1 liter at the temperature at which the titrations are to be made.. The bichromate solution should be checked against pure iron.

(b) DETERMINATION.

(1) Standardizing the sodium thiosulphate solution.—Place 20 cc. of the potassium bichromate solution, to which has been added 10 cc. of the solution of potassium iodide in a glass-stoppered flask. Add to this 5 cc. of strong hydrochloric acid. Allow the solution of sodium thiosulphate to flow slowly into the flask until the yellow color of the liquid has almost disappeared. Add a few drops of the starch paste, and with constant shaking continue to add the sodium thiosulphate solution until the blue color just disappears.

(2) Weighing the sample.—Weigh about one-half gram of fat or 0.250 gram of oil* on a small watch crystal or in some other suitable way. Melt the fat, mix thoroughly, pour onto the crystal, and allow to cool. Introduce the watch crystal into a wide-mouth 16-ounce bottle with ground-glass stopper.

(3) Absorption of iodine in Hübl's method.—Dissolve the fat or oil in the bottle in 10 cc. of chloroform. After complete solution has taken place add 30 cc. of the iodine solution in the case of fats, or from 40 to 50† in the case of oils. Place the bottle in a dark place and allow to stand, with occasional shaking for three hours.‡ This time must be closely adhered

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* Use from 0.100 to 0.200 gram in the case of drying oils which have a very high absorbent power.

† F. Ulzer (J. Soc. Chem. Ind., 1898, 17: 276) says iodine should be in excess, about twice the amount that is absorbed. The solution loses strength with age, but can be used as long as 35 cc. of tenth-normal thiosulphate neutralize 25 cc. of iodine solution.

‡ The time allowed does not give the complete iodine absorption power of an oil or fat and cannot be compared with determinations in which six to twelve hours have been used. It gives very satisfactory comparative results, but the time factor must be very closely observed.

to in order to get good results. The excess of iodine should be at least as much as is absorbed.

(4) Absorption of iodine in Hanus method.—Add 25 cc. of the iodine solution to the chloroform solution of the fat. Allow to stand, with occasional shaking, for thirty minutes. The excess of iodine should be at least 60 per cent. of the amount added.

(5) Titration of the unabsorbed iodine.—Add 10 cc. of the potassium iodide solution in the Hanus method, or 20 cc. in the Hübl method and shake thoroughly, then add 100 cc. of distilled water to the contents of the bottle, washing down any free iodine that may be noted on the stopper. Titrate the iodine with shaking, until the yellow color of the solution has almost disappeared. Add a few drops of starch paste and continue the titration until the blue color has entirely disappeared. Toward the end of the reaction stopper the bottle and shake violently, so that any iodine remaining in solution in the chloroform may be taken up by the potassium iodide solution.

(6) Standardizing the iodine solution by thiosulphate solution.—At the time of adding the iodine solution to the fat employ two bottles of the same size as those used for the determination for conducting the operation described under paragraphs (3), (4) and (5), but without the presence of any fat. In every other respect the performance of the blank experiments should be just as described. These blank experiments must be made each time the iodine solution is used. Great care must be taken that the temperature of the solution does not change during the time of the operation, as acetic acid and alcohol have very high coefficients of expansion, and a slight change of temperature makes an apprecible difference in the strength of the solution.

Per cent. of iodine absorbed.

Weight of fat taken	gram	0.290
Quantity of iodine solution used	cc.	40.0
Thiosulphate equivalent to iodine used	cc.	65.0
Thiosulphate equivalent to remaining iodine	cc.	40.0
Thiosulphate equivalent to iodine absorbed	cc.	25.0

Per cent. of iodine absorbed (25.0 x 0.012692 x 100) divided by 0.250=126.92.

Standard Specifications for Purity of Boiled Linseed Oil from North American Seed.

American Society for Testing Materials (1915).

I. PROPERTIES AND TESTS.

Boiled linseed oil from North American seed shall conform to the following requirements:

	Maximum.	Minimum.
Specific Gravity at $\frac{15°.5}{15°.5}$ C.	0.945	0.937
Acid Number	8	.....
Saponification Number	195	189
Unsaponifiable Matter, per cent	1.5	.....
Refractive Index at 25° C.	1.484	1.479
Iodine Number (Hanus)	.....	178
Ash, per cent	0.7	0.2
Manganese, per cent	.....	0.03
Calcium, per cent	0.3	.....
Lead, per cent	.....	0.1

II. METHODS OF TESTING.

The recommended methods of testing are as follows:

General.—The sample should be thoroughly agitated before the removal of a portion for analysis.

Specific Gravity.—Use a pyknometer, accurately standardized and having a capacity of at least 25 cc., or any other equally accurate method, making a test at 15° .5 C., water being 1 at 15° .5 C.

Acid Number.—Expressed in milligrams of KOH per gram of oil. Follow the method described in Bulletin No. 107, revised 1908, Department of Agriculture, Bureau of Chemistry, page 142.

Saponification Number.—Expressed as with Acid Number. Blanks should also be run to cover effect of alkali in glass. Follow method given in Bulletin No. 107, revised 1908, Department of Agricuture, Bureau of Chemistry, pages 137-138.

Unsaponifiable Matter.—Follow Boemer's method taken from his Ubbelohde Handbuch Der Ole u. Fette, pages 261-262 (as quoted on p. 338, under specifications for raw linseed oil).

Or, any accurate method involving the extraction of the dried soap may be used.

Refractive Index.—Use a properly standardized Abbé Refractometer at 25° C., or any other equally accurate instrument.

Iodine Number (Hanus).—Follow the Hanus method as described in Bulletin No. 107, revised 1908, Department of Agriculture, Bureau of Chemistry, page 136.

Ash.—The determination of the percentage of ash and the constituents thereof may be made by any method which gives accurate results.

CHAPTER XXIV.

THE APPLICATION OF PAINTS AND FINISHES TO WOOD.

Prepared paints, contained in sealed packages, are the most economical and convenient. The brand selected should be composed of pigment and liquid, the pigment being white lead (corroded or sublimed) admixed with zinc oxide, with or without a small amount of chemically inert pigments. These pigments should be ground in a liquid composed of linseed oil with a small amount of drier and thinner. Small amounts of color pigments have been added to such mixtures, if the paint is tinted. These paints are suitable for the exteriors of all wooden structures.*

If the painter desires to use a paint mixed by hand, paste paints may be obtained either in the form of white lead ground in oil or zinc oxide ground in oil, which may be mixed together, or purchased in the form of a Prepared Paste Paint made of these pigments. It is customary to add to 100 lbs. of a paste paint from 4 to 6 gallons of linseed oil and a pint of liquid drier. The mixture may be thoroughly stirred in a barrel or tub. Labor and time are necessary to produce a smooth paste. Loss by spattering should be avoided, if possible. A gallon or more of turpentine may be used to take the place of part of the oil for first-coat work. If a colored paint is desired, color ground in oil may be added to produce the desired result. The paint should then be stirred for a long period in an endeavor to get the color thoroughly into the mass in order to prevent streaking.

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* *U. S. Army Paints (White).*

The majority of the high-grade paints to be purchased from reliable dealers will closely approximate the prepared paint called for by the specifications of the U. S. Army, which are as follows:

"The paint must be furnished in prepared form, ready for application. White paint must contain not less than 65 per cent nor more than 70 per cent of pigments, the balance to be liquids. The liquids shall consist of pure raw linseed oil, containing a total of not over 10 per cent. of turpentine and turpentine drier. The pigment portion of the paint shall consist of white lead (basic carbonate or basic sulphate) and zinc oxide. There shall not be less than 25 per cent. nor more than 50 per cent. by weight of zinc oxide. Paints of this composition containing, in addition, not over 15 per cent. by weight of such white pigments as barytes, china clay, whiting, asbestine, and silica will be accepted under these specifications."

Selection of Color.—The color of a paint to be selected for a house requires consideration. In many rural localities, white paints are used, and they contrast pleasantly with the green of the surrounding foliage. It must be remembered, however, that white paints which have been tinted, by grinding into them small percentages of permanent colors, are more economical to use, since the wearing value of these tinted paints is from 30% to 60% greater than the wearing value of white paints. For instance, if a white paint is applied to one house and a similar white paint, tinted with say

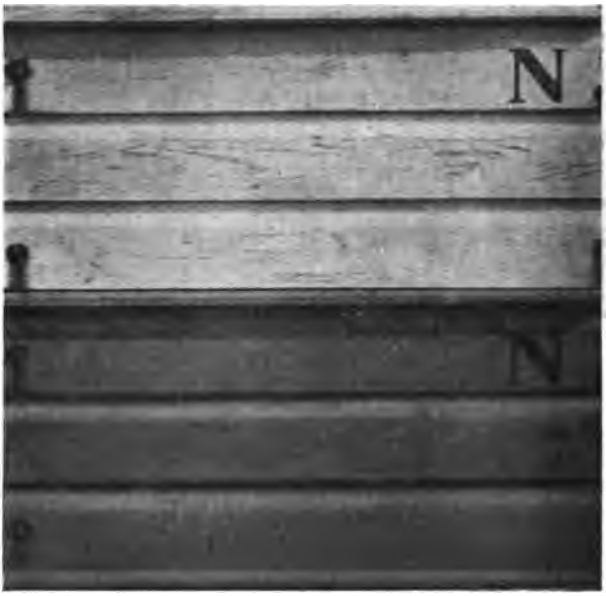

Fig. 143.

In the above illustration there are shown two painted panels which have been exposed for nearly three years to severe weather conditions. The paint tinted gray, which was applied to the lower panel, was of the same composition as the white paint applied to the upper panel. The superior condition of the gray paint is clearly shown.

3% or 4% of color, is applied to another house in the same locality at the same period of time the surface painted white will probably require repainting at the end of a period of three years, while the surface painted with the colored paint will be in an excellent state of preservation and will probably not require repainting for two more years. Therefore tinted paints should be used whenever durability is the commanding consideration. The property owner should also remember that the lighter shades or tints are in many instances best adapted, since the lighter colors reflect the heat rays from the sun, while the darker colors, such as dark red, dark blue and very dark gray, absorb the heat. For this reason, a house painted in light colors will be cooler in the summer than one painted in very dark colors.

Full directions for use usually appear upon all packages of prepared paints. However, in case such directions are lacking, the following general directions will be found useful.

Before the paint is applied, the wooden surface must be freed from moisture. If new, weathering of the wood for a short period is generally advisable in order to allow thorough seasoning and drying-out of absorbed moisture. Painting should never be done in damp weather. A successful job depends upon the application of the paint during clear dry days. If the wood has not been painted before, any visible sap streaks or knots should be brushed with turpentine just before applying the paint. Do not use shellac for priming knots. The turpentine treatment will soften the resin in the wood and allow the priming or first coat of paint to soak thoroughly into and combine with the resin, thus preventing scaling. For the priming coat, there should be added to a gallon of prepared paint from 1 to 3 pints of turpentine (*or benzol* when obtainable*). The mixture should be thoroughly stirred until it is uniform throughout. It may then be applied by brushing out to a thin coat on the new wood. The turpentine will serve to carry the paint into the pores of the wood, and thus provide a good, substantial bond. The paint, moreover, will dry rapidly to a hard surface which will provide a permanent foundation for subsequent coats. Upon the priming coat depends the success of the whole painting job. Even if the coat looks thin, the hiding power of the paint should be sacrificed in order to obtain this thorough penetration and hard drying. Never use ochre as a priming coat, serious results are bound to follow.

---

* Benzol 90 degrees or benzol 160 degrees (solvent naphtha) may be used with even better results than turpentine for thinning the priming coat of paint. Benzol is the water-white distillate from coal tar. It must not be confounded with benzine. When benzol is not obtainable, use turpentine.

When the priming coat has become thoroughly hard and dry, which, as a rule, will take at least three days, although a week is better, all the nail holes and other imperfections in a wooden surface may be closed up with putty. There may then be applied the second coat of paint as it comes from the container, without the addition of any material except a small quantity of turpentine if the paint is heavy. One pint of turpentine to a gallon of paint is generally sufficient for this purpose. The turpentine will cause the second coat to dry with a semi-matte surface. After a suitable drying period, the third coat may then be applied. No turpentine or thinner should be added to the third coat of prepared paint, since it is desired to obtain a film rich in oil, that will dry to a high-gloss surface. When desired an additional coat may be applied.

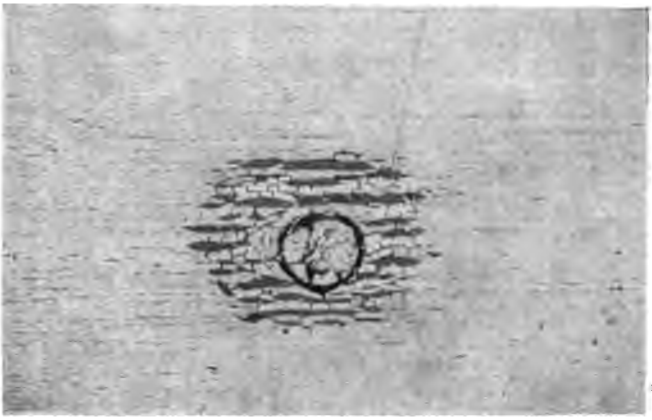

FIG. 144.

Result of Shellacking Knots.

It should be remembered that more enduring results follow the application of a number of thin coats. When old surfaces are to be repainted, all loose, scaled paint should be removed and rough, checked surfaces lightly sanded with fine sandpaper. The work may proceed as for the second and third coats for new surfaces.

Interior Painting.—Clean and sandpaper. Brush-coat knots and sappy spots with turpentine not more than one hour previous to the application of the first coat of paint. To one gallon of paint there should be added one to two pints of turpentine The thoroughly stirred mixture should then be applied, brushing it out into a thin coat. This will rapidly dry to a hard undercoating that has penetrated deeply into the wood. If the finishing color is to be white or light tinted, there should be applied over the priming coat of paint a thin coat of white shellac. This will prevent discoloration of the surface by resin in the wood. After drying, the imperfections may be puttied up. There should then be applied three coats of paint of the desired color. If a varnish coat is applied over the paint, it should be a light-colored, good-wearing varnish, evenly applied, and it should be colored with the finishing tint.

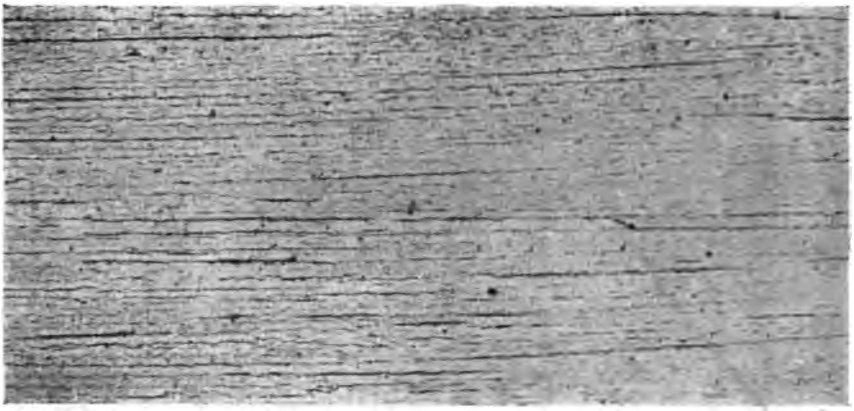

FIG. 145.

Two-coat Work After Four Years' Exposure.

Enameling.—For enameling, the same treatment of knots, priming with paint, coating with shellac, and puttying should be adopted. Then apply three coats of white prepared paint or flat finish. Then apply one coat of half paint and half enamel. Finish with one full-flowing coat of best enamel. Each coat must be thoroughly dry, and should be lightly sandpapered before the application of another. All coats should be tinted as desired. The enamel coats may be rubbed with water and powdered pumice stone if a satin finish is desired.

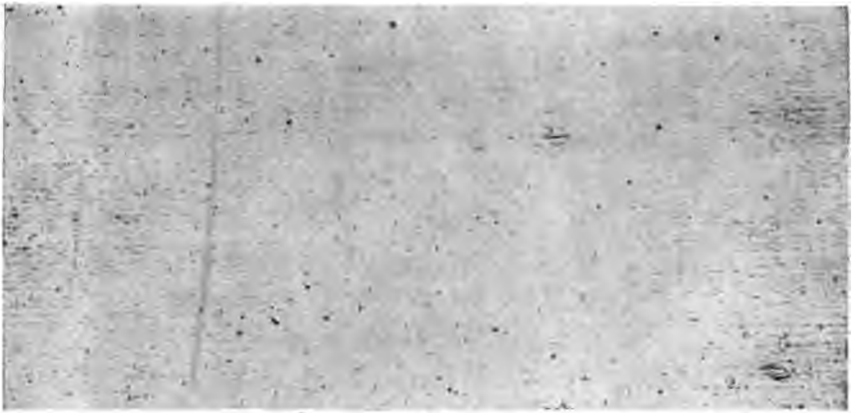

FIG. 146.

Three-coat Work After Four Years' Exposure—Same Paint as in Fig. 145.

Staining and Varnishing.

Natural Finish.—The woodwork should be thoroughly cleaned and sandpapered where necessary. Apply one coat of white shellac.

Cover all nail holes and other imperfections with putty colored to match the wood, taking care to remove surplus putty.

Give two coats of good-wearing body varnish, the last coat to be evenly flowed on. Sandpaper thoroughly between coats. If a flat finish is desired, the varnish coats may be rubbed—not too closely—to a dull, even finish, or a dull-finish varnish may be used. If the natural color of the wood is a trifle too bright for the effect desired, a very little burnt sienna added to the first coat of varnish will produce a more suitable finish.

Stained Work.—All woodwork should be thoroughly cleaned and free from imperfections. Apply one coat of linseed oil prepared stain.* Sandpaper lightly. Close nail holes with putty to match stain, removing all excess putty. Apply two good coats of strong-wearing body varnish, evenly flowed on, and sandpaper lightly between coats, taking care that each coat is thoroughly dry before another is applied. For a flat surface rub lightly with oil and pumice stone or apply one coat of flat varnish.

Finishing Floors.

Natural Color Finish.—Floors should be cleaned, smoothed, hand-scraped, and sandpapered with the grain of the wood, and left in perfect condition to receive the work of the painter.

Apply a very thin first coat of white shellac. Sand lightly with fine sandpaper, and apply two coats of best elastic floor varnish. If a dull finish is desired, rub lightly with oil and pumice stone. Wax varnished surface if desired.

Stained Floors.—If the floor is to be stained, omit the shellac and apply one coat of linseed oil prepared stain. When dry, apply two coats of best elastic floor varnish. Wax if desired.

Do not attempt to finish a floor by the use of wax or oil alone. A polished surface will result, but it will not be hard, and will soon discolor with dust and dirt.

Painting Shingle Roofs.—New shingles, if well seasoned, may be dipped in a prepared mineral paint that has been suitably thinned with turpentine or mineral spirits so that the excess paint will readily run off, leaving an even film. It is customary, however, to paint shingles on the roof. This is usually done after the shingles have weathered for a short period of time, but previous to the formation of corner pockets or other defects due to the action of the weather. The paint should be well brushed in. One coat is sufficient, but two coats will give a more durable job. Shingles 4 inches in width are usually laid to show not over 4½ inches of their length of 16 inches, thus forming a quadruple roof of approximately 100 square feet to a thousand shingles. One gallon of prepared shingle paint will cover 400 square feet, one coat, if well brushed out.

---

*Stains containing benzol penetrate better than other stains.

Painting Plaster Walls and Ceilings.—A few years ago the use of paint was largely confined to exteriors of buildings. Interior walls were often left bare. Discoloration and dampness followed. The modern method is to decorate all interior wall and ceiling surfaces with paints which are of a washable character. These paints may present either a flat and light-diffusing surface, or a high-gloss, enamel-like surface. The flat or high-gloss paints are obtainable in prepared form. Before applying such paints to plaster or cement-wall surfaces, a wash treatment with a 25% water solution of zinc sulphate is advisable, in order to neutralize the lime present in the wall. Later, when the walls are thoroughly dry, the paints should be applied in two or three-coat work. High-gloss paints should always be applied over an under-coat of flat paint. Light cream color and the very light shades of pink, green, and blue are the tints which give the greatest amount of light reflection in a room.

Painting Costs.—Paste paints cost about $3.00 to $4.00 per gallon, while prepared paints sell for $2.25 to $2.75 per gallon. A paint in prepared form, ready for application, will cover from 300 to 1,400 sq. ft. per gallon, depending upon the character of surface to which it is applied. On smooth iron surfaces, the greatest spreading rate is obtained, and on rough concrete surfaces, the lowest spreading rate. On wooden surfaces the average spreading rate is about 900 sq. ft. per gallon, one coat. In estimating the amount of paint required for a surface, the total number of square feet should be calculated by multiplying the width by the height, of each side. The total area should then be divided by 300, which will give approximately the number of gallons required to produce three-coat work. For instance, if the total area for the four sides of a house is 6,300 sq. ft., 21 gallons of paint will be required for the work. If the cost of the paint is $2.35 per gallon, the material cost will be $49.35. The cost of labor for properly applying the paint should be figured at double

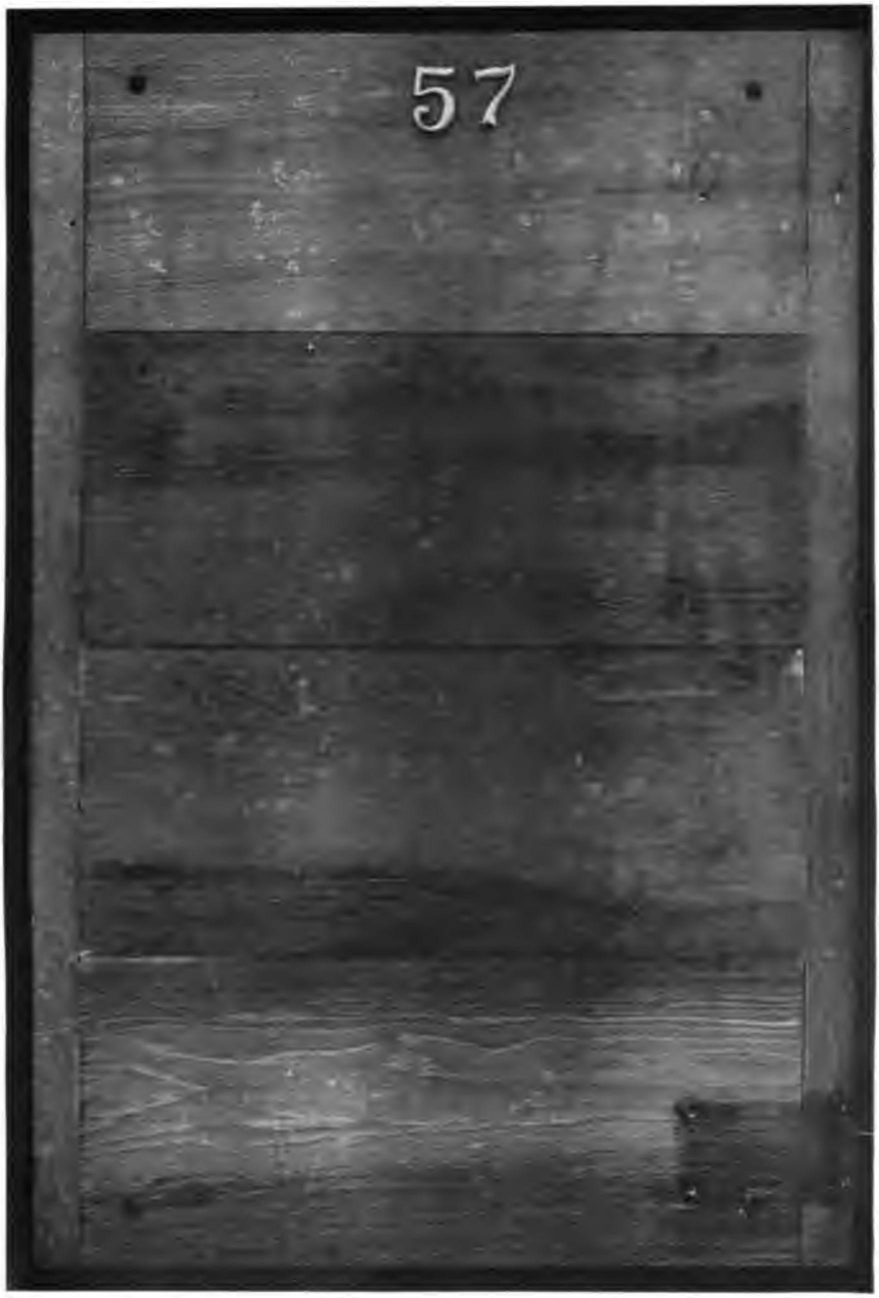

FIG. 147.

Unpainted Wood After Three Years' Exposure.

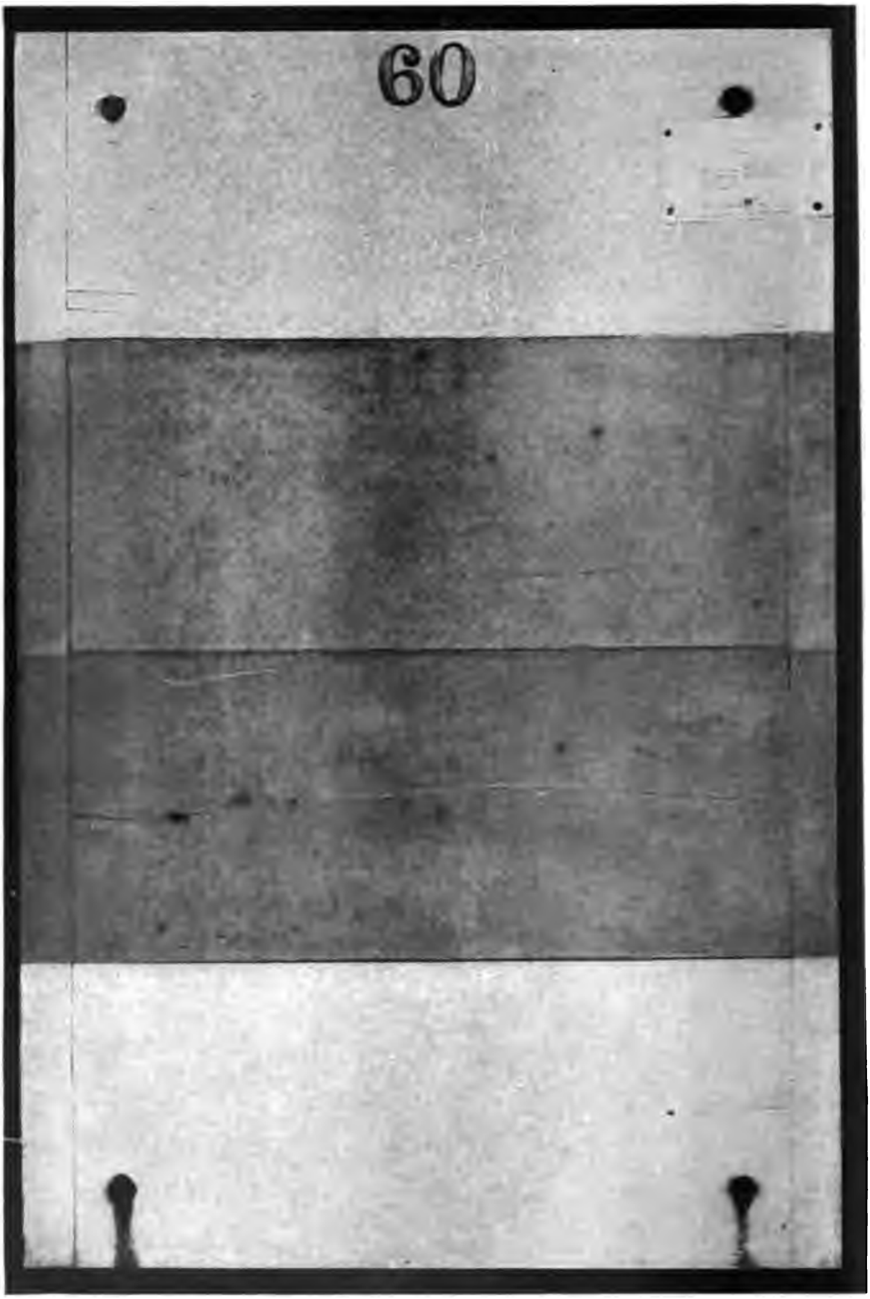

FIG. 148.

Painted wood after three years' exposure. The boards were painted white, yellow, gray, and light blue. Excellent maintenance of color was shown.

the cost of the paint. To the total must be added cost of brushes, ladders, incidental materials, etc. It is readily seen, therefore, that the cost of the paint is a small part of the cost of painting, and for this reason only the best paint should be used in order to secure a job that will last for the longest time without repainting.

Economy of Painting.—The property owner should remember that it is a very good business proposition to keep buildings of all types, especially dwellings and farm buildings, well painted. By so doing, the value of a property increases at least 25%. If wooden structures are left bare and exposed, the surfaces become roughened and the wood is subjected to warping and cracking. When dampness enters such exposed wood, conditions become favorable for the action of destructive fungi and rotting may take place. Application of good paint, however, will preserve wood almost indefinitely, since it closes the openings and prevents the admittance of decay-producing organisms.

Even more striking illustrations of the truth of this statement are afforded by the condition of those well-painted, century-old dwellings to be found throughout the original colonies of this country. Some of these are shown in Figs. 149-155.

Moreover, paints not only decorate and preserve wood, but they make it more resistant to fire. For this reason, the application of paints to shingled roofs is often advisable. For instance, prepared paints containing 60% to 70% of non-combustible, metallic or mineral pigments, may be termed fire-resisting. When such paints are applied to shingles a very water-proof semi-metallic film results. The film smooths the rough, fuzzy surface of the wood and prevents warping at the edges, thus doing away with the formation of pockets in which hot cinders, blown from a passing locomotive or carried from a neighboring fire, might lodge.

Paints for Various Surfaces.—Painting the exterior or interior walls of a dwelling constitutes only a part of the many uses for paint. Painting metals of various kinds, varnishing and staining woodwork, and many other applications call for the use of an immense variety of paints and finishes. A list of many of these is shown in the chart on page 363.

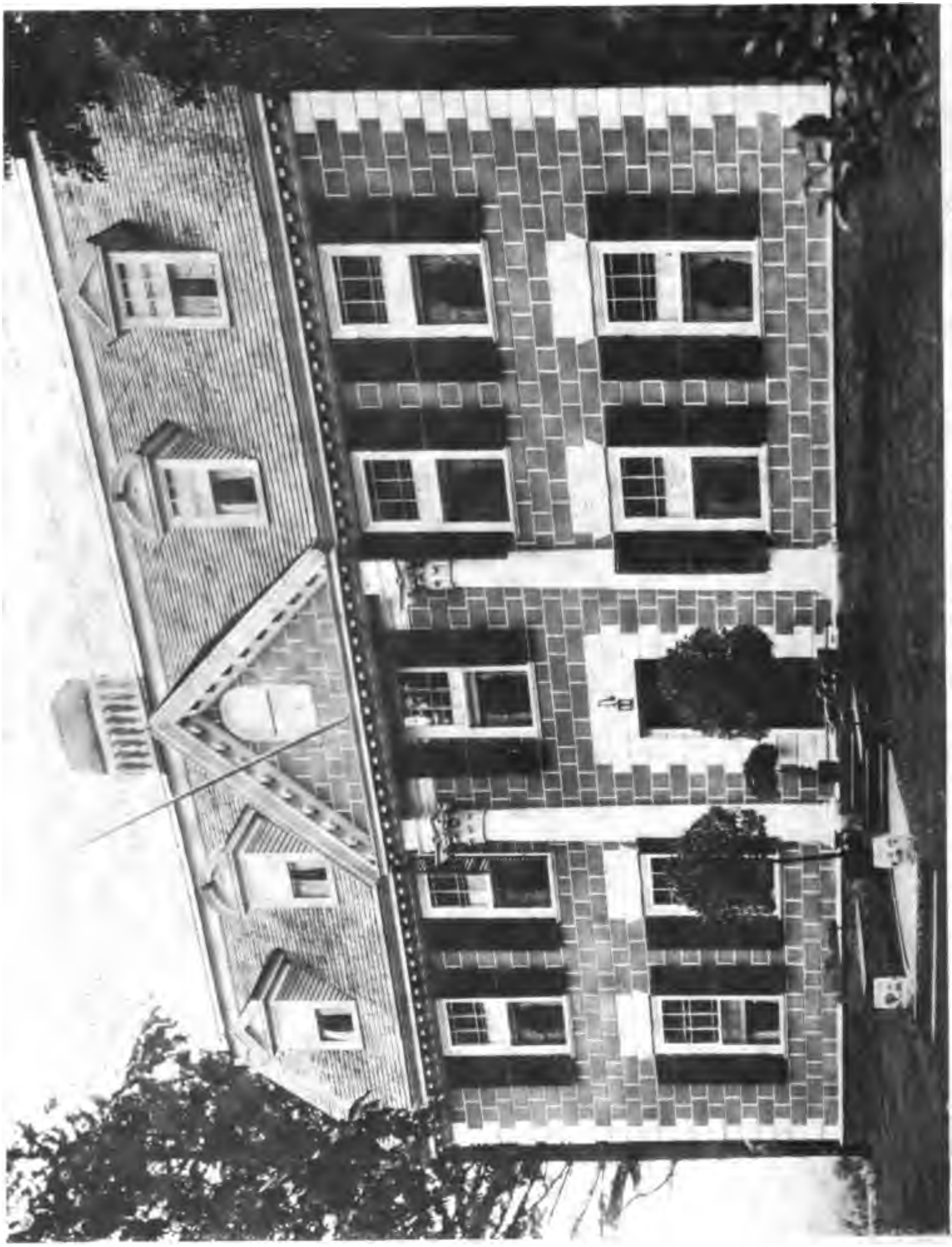

FIG. 149.--The Lindens--Danvers, Mass. Built in 1770.
Used as Headquarters for General Gage. The wood is painted to resemble stone construction.

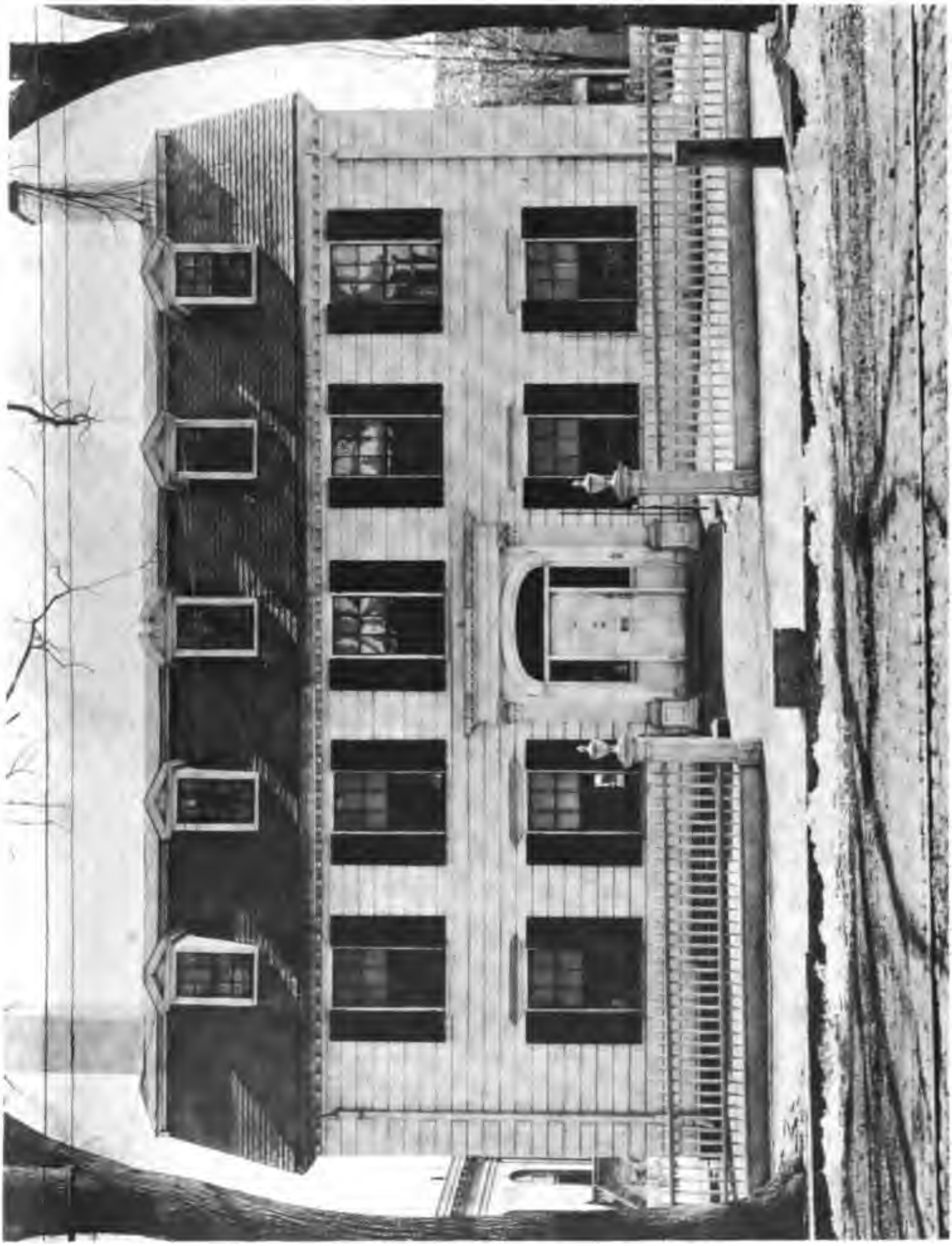

Fig. 150.—Tristram Dalton House—Newburyport, Mass. Built in 1720.

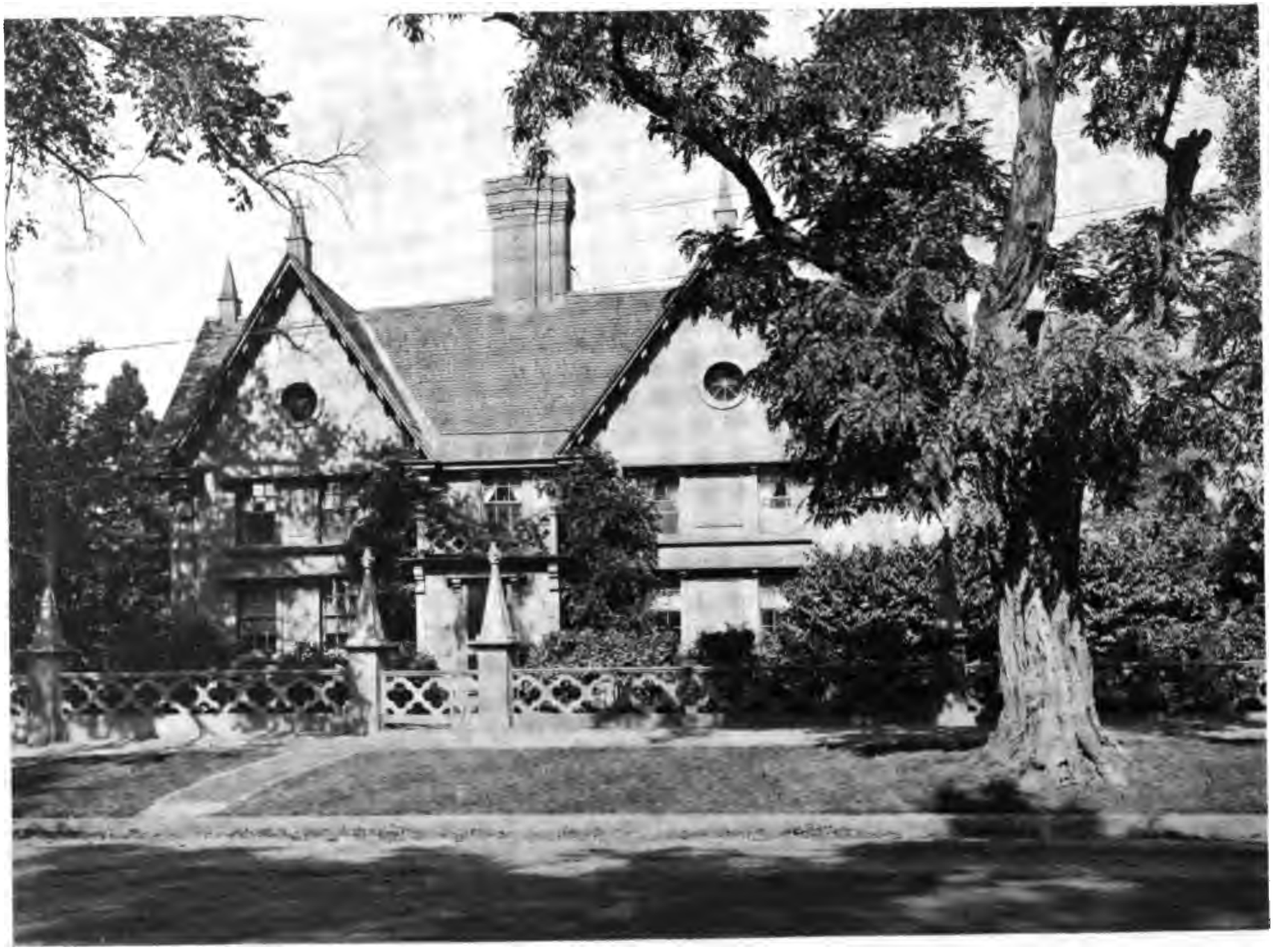

FIG. 151.—Pickering House—Salem, Mass. Built in 1650.
Among its occupants was Timothy Pickering, Quartermaster General Continental Army.

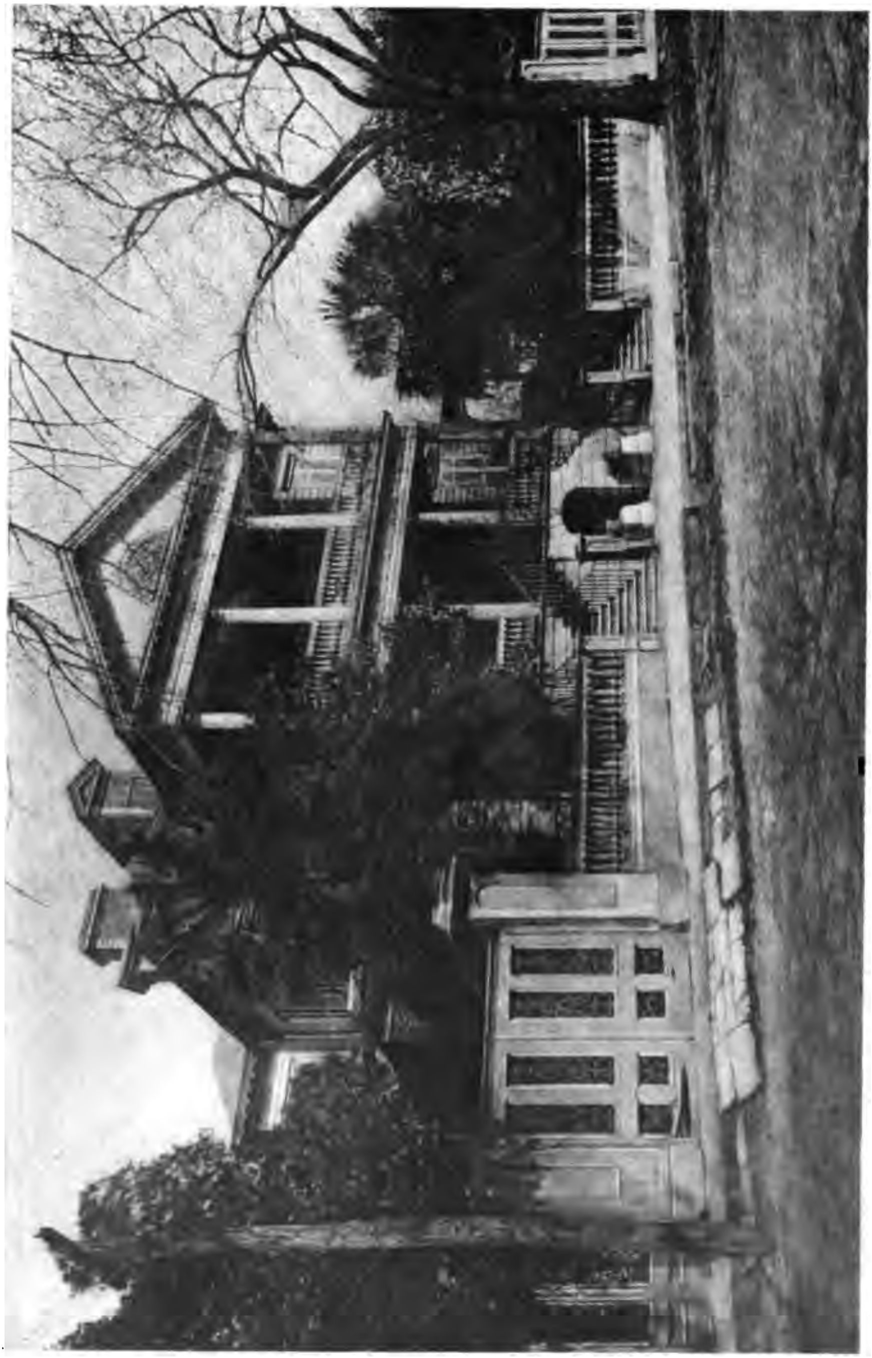

Fig. 152.—Bennett Mansion—Charleston, S. C. Built about 1820.

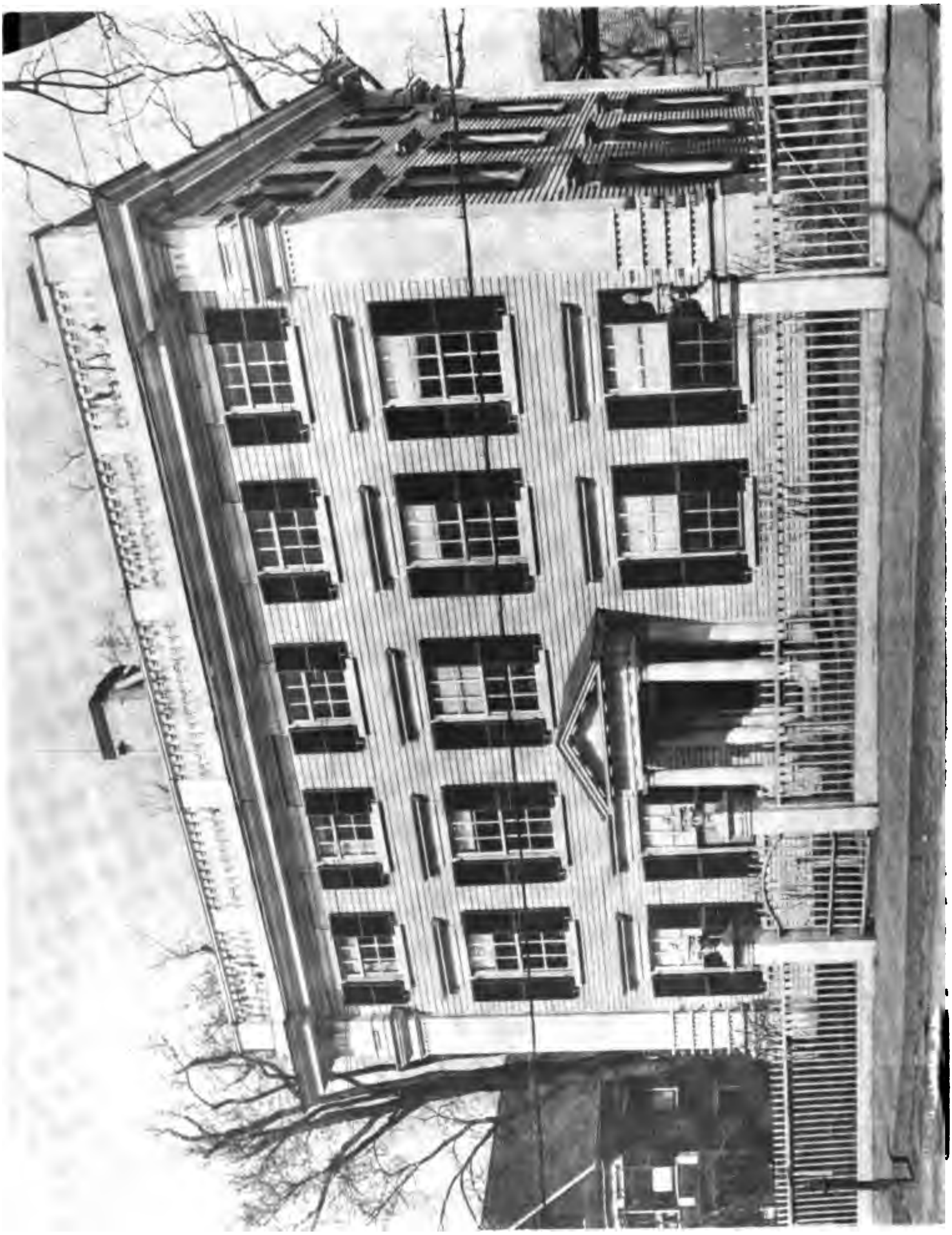

FIG. 153.—Nichols House, Salem, Mass. Built in 1782.

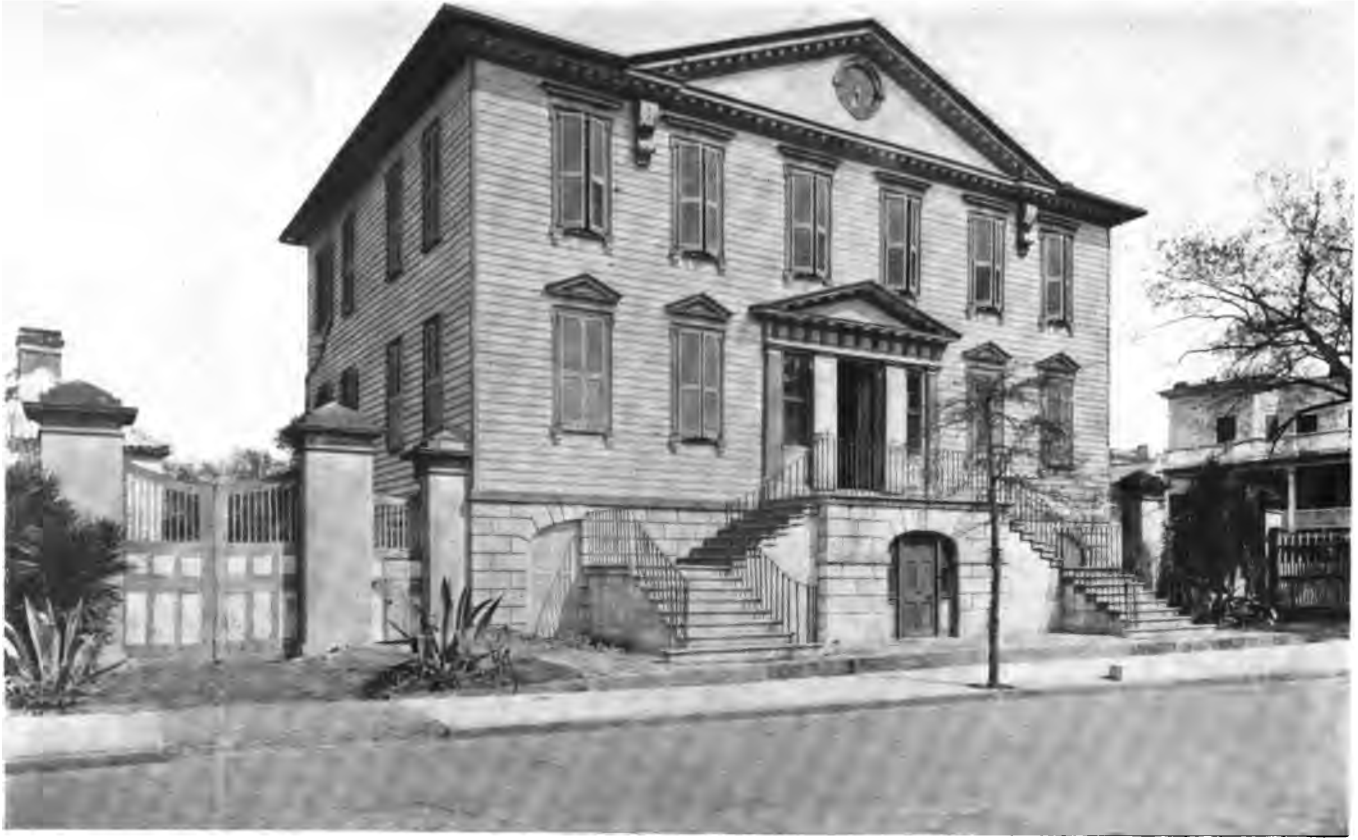

FIG. 154.—Sloan Residence—Charleston, S. C. Built in 1763.

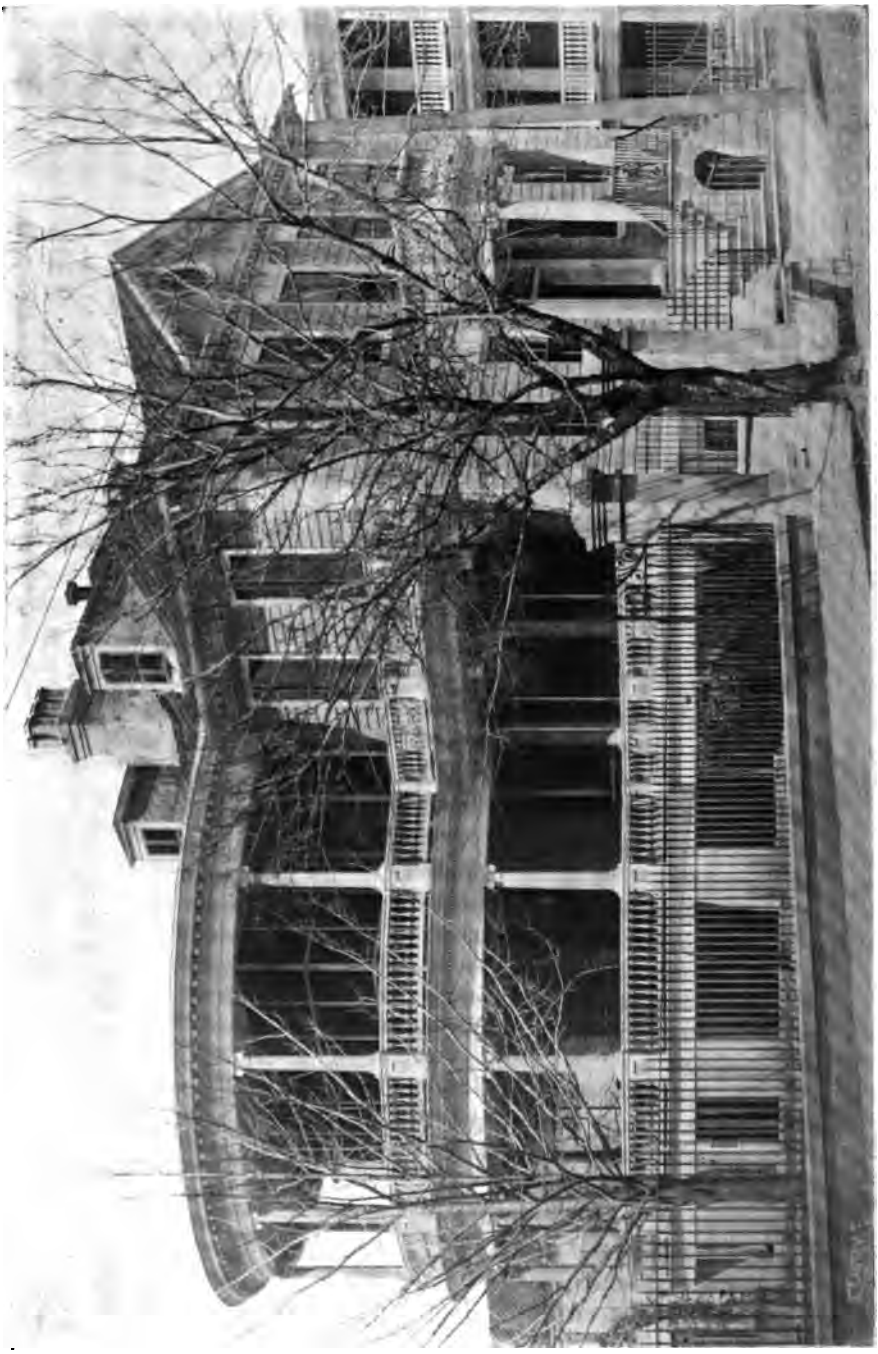

FIG. 155.—G. W. Williams' Residence—Charleston, S. C. Built by John Edwards, 1770.

Paints for Various Purposes.

PAINT FOR EXTERIOR SURFACES	**WOOD**	**Weatherboarded Dwellings, Churches and Factories, Fences and Wooden Structures.**	**Paint prepared on a Lead and Zinc Base. Preferably tinted. Class "A."**
		Shingled Roofing and Siding.	**Same as Class "A" or a Creosote Shingle Stain.**
		Sheds, Barns and Outbuildings.	**Same as Class "A" or Prepared Iron Oxide Paint.**
		Porch Floors.	**Colored Floor Paint containing Durable Varnish.**
		Window Shutters.	**Same as Class "A" or Chrome Green Shutter Paint.**
	METAL	**General Structural Iron and Steel Girders, Roofing, Siding, etc.**	**Rust Inhibitive Prepared Paint, Red Lead, Iron Oxide, etc. Class "B."**
		Galvanized Iron.	**Prime with 5% Water Solution of Copper Salt. Dry and apply Class "B" Paint.**
		Tinned Roofing and Copper Flashing.	**Clean all grease with Benzene. Apply Class "B" Paint.**
	STONE	**Brick Walls and Fronts.**	**Same as Class "A" or Prepared Red Iron Oxide Paint.**
		Cement and Concrete Structures, Ball Parks, Pavilions, Stucco on Brick or Frame, Cement Tanks, Posts, Silos, Culverts, etc.	**Prime with 25% Water Solution of Zinc Sulphate (to neutralize alkali). Dry and apply Class "A" Paint or Cement Coater.**
PAINT FOR INTERIOR SURFACES	**WOOD**	**General Trim, Stairways, Doors, Paneling.**	**Class "A" Paints finished with Enamel or Varnish.**
		Doors, Paneling, Floors, etc. Transparent finish.	**Fillers, Stains and Varnish as desired.**
	METAL	**Same as for Exterior Work.**	**Same as for Exterior Work.**
	STONE	**Ceilings and Walls of Portland Cement, Keene Cement or Sand Lime Plaster.**	**Alkali Neutralizing Primer, then Sanitary Flat Finish Oil Paint.**
		Ceilings and Walls of Bath-rooms and Kitchens.	**Alkali Neutralizing Primer, then Class "A" Paint, and Varnish or Washable Enamel.**
		Cement Floors.	**Alkali Neutralizing Primer, then Class "A" or Prepared Floor Paint.**

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